ORIGINAL RESEARCH

The conformational spaces of dinaphthyl ketones, dinaphthyl thioketones, and dinaphthyl diazomethanes: 1-substituted naphthalenes versus 2-substituted naphthalenes

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Abstract 1,1'-Dinaphthyl ketone (15), 1,2'-dinaphthyl ketone (18), 2,2'-dinaphthyl ketone (19), 1,1'-dinaphthyl thioketone (16), 1,2'-dinaphthyl thioketone (20), 2,2'-dinaphthyl thioketone (21), 1,1'-dinaphthyldiazomethane (17), 1,2'-dinaphthyldiazomethane (22), and 2,2'-dinaphthyldiazomethane (23) have been synthesized. Ketone 15 has been prepared from di(1-naphthyl)methanol; ketone 18 has been prepared by a Friedel-Crafts acylation of naphthalene with 2-naphthoyl chloride; ketone 19 has been prepared by a Grignard reaction of 2-naphthylmagnesium bromide with 2-naphthoyl chloride. Thioketones 16, 20, and 21 have been prepared by reactions of the corresponding ketones 15, 18, and 19 with Lawesson's reagent. The diazomethane derivatives 17, 22, and 23 have been prepared by the HgO oxidation of the respective hydrazones 25, 27, and 28 (prepared from the respective thicketones 16, 20, and 21). The crystal and molecular structures of ketones 15, 18, and 19 and of thioketone 16 have been determined. A variety of conformations in the crystal structures is noted: 1Z, 1'Z (15), 1E, 1'Z (16), 1E, 2'E (18), $2Z_{2}/2$ (19). The NMR experiments have demonstrated the downfield shifts of the protons peri to the carbonyl and the thiocarbonyl groups in 15, 16, and 18, but not in 20. A systematic DFT study (B3LYP/6-31G(d)) of the conformational spaces of 15-23 and their ¹H and ¹³C NMR chemical shifts has been performed. In each series

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of constitutional isomers, the order of stabilities is $2,2'-(NA)_2C=X > 1,2'-(NA)_2C=X > 1,1'-(NA)_2C=X$. The decrease in the stabilities of 1-naphthyl derivatives relative to 2-naphthyl derivatives is attributed to the increased overcrowding and the increased twist angles in 1-naphthyl derivatives. The increased stabilization of *E*-conformations with the increase of the radius of a heteroatom at C⁹ due to the steric reasons is noted. The DFT calculations satisfactorily describe the X-ray conformations of **15**, **16**, **18**, and **19**.

Keywords X-ray crystallography \cdot Structure \cdot DFT \cdot NMR \cdot Conformation \cdot *Peri*-interactions

Introduction

Naphthalene (1) is the simplest polycyclic aromatic hydrocarbon (PAH) [1]. One of the features that distinguish naphthalene from benzene (2) is the peri relationship between the neighboring positions 1 and 8 (and between the neighboring positions 4 and 5), which is characteristic of naphthalene and is absent in benzene [2]. The peri relationship differs significantly from the ortho relationship between the neighboring positions in benzene, e.g., 1 and 2 and 1 and 6. The C^1-H^1 and C^8-H^8 bonds in naphthalene are parallel, while the C^1-H^1 and C^2-H^2 bonds in benzene and in naphthalene form an angle of 60°. The geometrical constraint in naphthalene affects the non-bonding distances r(X···X) in 1,8-di-X-naphthalene (3) versus 1,2-di-Xnaphthalene (4) and 2,3-di-X-naphthalene (5). In unsubstituted naphthalene (1) (when X = H in 3 and 4), $r(H^1 \cdots H^8) = 245 \text{ pm while } r(H^1 \cdots H^2) = 249 \text{ pm } [3]. \text{ In } 3,$ $r(X^1 \cdots X^8)$ is much more sensitive to the nature of the substituent X than $r(X^1 \cdots X^2)$, $r(X^2 \cdots X^3)$, $r(X^1 \cdots H^2)$,

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 $r(X^2 \cdots H^1)$, and $r(X^2 \cdots H^3)$ in 4 and 5. For example, a comparison of the C-Cl bond lengths of 1,8-dichloronaphthalene (6) with those of 1,2-dichloronaphthalene (7)and 2.3-dichloronaphthalene (8) shows that at B3LYP/6-31G(d), $\Delta r(peri) = r(Cl^1 \cdots Cl^8) = 310.9$ pm in 6, while $\Delta r(ortho) = r(Cl^1 \cdots Cl^2) = 318.6 \text{ pm in 7 and } \Delta r(ortho) =$ $r(Cl^2...Cl^3) = 321.7 \text{ pm}$ in **8**. These differences are reflected in the corresponding relative Gibbs free energies $\Delta G_{298} = 29.19$ (6), 1.74 (7), 0.00 kJ/mol (8). The implications of the peri versus ortho relationships are also expressed in 1-substituted naphthalenes, as compared with 2-substituted naphthalenes. The effect of interactions between substituents at the peri positions in naphthalenes has been reviewed [4]. A recent relevant illustration is a series of glass-forming materials based on the 1,3,5tris(naphthyl)benzene motif [5, 6]. The study revealed a conformational-behavior dependence on the site of substitution (1 vs. 2) at the naphthalene rings [5, 6].



In the course of our studies of overcrowded bistricyclic aromatic enes (BAEs) (Fig. 1) [7, 8], we have recently devoted our attention to naphthologous analogues of BAEs [9]. The BAEs are overcrowded in their *fjord* regions [8] on both sides of the central double bond ($C^9=C^{9'}$). The bridges X and Y in BAEs have a profound effect on the overcrowding, dynamic stereochemistry and thermochromism of these fascinating systems [7, 8, 10-12]. The degree of overcrowding in BAEs may be reduced by removing the bridges X and/or Y. Such removals, which cancel the *fiord* region(s), may be realized by the following two variations leading to open-BAEs; (i) removal of one bridge (X or Y) of BAE to give BAE-1, i.e., mono-bridged tetraarylene, e.g., 9-(diphenylmethylene)-9H-fluorene (9); (ii) removal of the two bridges of BAE to give BAE-2, i.e., tetraarylene, e.g., tetraphenylethene (10). In BAE-1 and BAE-2, in contrast to BAE, there are prima facea essentially "free" rotations around the single C-C bonds between the ene carbon atoms (C^9 and/or $C^{9'}$) and the aryl groups bonded to C^9 and/or $C^{9'}$. This effect confers a conformational flexibility, which may result in a reduction in the degree of overcrowding. We have recently reported the syntheses, molecular and crystal structures and NMR spectroscopic study of the following naphthologous analogues BAEs-1: 9-(di-1-naphthalenylmethylene)-9H-fluorene (11) and 9-(di-1-naphthalenylmethylene)-9H-xanthene (12) [9]. The syntheses of **11** and **12** started from 1,1'-dinaphthyl ketone (**15**), 1,1'-dinaphthyl thioketone (16), and bis(1-naphthyl)diazomethane (17). The DFT computational study of the conformational spaces of 11 and 12 and their constitutional isomers, 9-(di-2-naphthalenylmethylene)-9H-fluorene (13) and 9-(di-2-naphthalenylmethylene)-9H-xanthene (14) were also reported [9].



In view of the differences between 1-substituted naphthalenes and 2-substituted naphthalenes (vide supra), it seemed worthwhile to compare the effect of the substitution site of naphthalene (1) on the conformational spaces of dinaphthyl ketones, dinaphthyl thioketone, and dinaphthyl diazomethanes. We report here the synthesis, a DFT

Fig. 1 Overcrowded BAEs. X = Y: homomerous; $X \neq Y$: heteromerous



computational study, an X-ray study and an ¹H-NMR and ¹³C-NMR spectroscopic study of the following naphthalene derivatives: 1,1'-dinaphthyl ketone (**15**), 1,2'-dinaphthyl ketone (**18**), 2,2'-dinaphthyl ketone (**19**), 1,1'-dinaphthyl thioketone (**16**), 1,2'-dinaphthyl thioketone (**20**), 2,2'-dinaphthyl thioketone (**21**), 1,1'-dinaphthyl diazomethane (**17**), 1,2'-dinaphthyldiazomethane (**22**), and 2,2'-dinaphthyldiazomethane (**23**).



Experimental

Melting points are uncorrected. All NMR spectra were recorded with a Bruker DRX 500 spectrometer; ¹H-NMR spectra were recorded at 500.2 MHz using CDCl₃ as solvent and as internal standard (Δ (CHCl₃) = 7.26 ppm). ¹³C-NMR spectra were recorded at 125.78 MHz using CDCl₃ as solvent and as internal standard (δ (CDCl₃) = 77.00 ppm). Complete assignments were made through 2-dimensional correlation spectroscopy (DQF-COSY, HSQC, and HMBC). IR spectra were recorded with a Bruker ALPHA spectrometer, using CHCl₃ as a solvent. Petroleum ether (PE, b.p. 40–60 °C), benzene, and diethyl ether for the Grignard reaction were dried on sodium and freshly distilled. In the rest of the experimental part benzene and toluene were dried on sodium, CH₂Cl₂ was dried on CaCl₂.

The X-ray study was carried on a Bruker SMART APEX CCD X-ray diffractometer equipped with a graphite monochromator. Single crystals of ketones 15 and 16 were attached to glass fibers, with epoxy glue, while these of 18 and 19 were attached with a mineral oil. The temperature of the crystals of 18 and 19 was maintained at -100 °C with a Bruker KRYOFLEX nitrogen cryostat. The system was controlled by a Pentium-based PC running the SMART software package [13]. Data were collected for each crystal using MoK α radiation ($\lambda = 0.71073$ Å). Immediately after collection, the raw data frames were transferred to a second PC computer for integration and reduction by the SAINT program package [14]. The structures were solved and refined by the SHELXTL software package [15]. Crystallographic data are summarized in Table 1.

1,1'-Dinaphthyl ketone (15)

Ketone 15 was prepared from di(1-naphthyl)methanol (24), as previously described [9]. A single crystal of 15 was obtained from CH_2Cl_2 .

¹H-NMR δ (CDCl₃), ppm: 7.440 (t, ³*J* = 8.0 Hz, ³*J* = 7.5 Hz, 2H, H³, H^{3'}), 7.575–7.600 (m, 4H, H⁶, H^{6'}, H⁷, H^{7'}), 7.616 (dd, ³*J* = 7.0 Hz, 2H, H², H^{2'}), 7.954 (ddd, ³*J* = 6.5 Hz, ³*J* = 7.0 Hz, 2H, H⁵, H^{5'}), 8.033 (d, ³*J* = 8.0 Hz, 2H, H⁴, H^{4'}), 8.576 (ddd, ³*J* = 9.0 Hz, 2H, H⁸, H^{8'}). ¹³C-NMR δ (CDCl₃), ppm: 124.34 (C³, C^{3'}), 125.89 (C⁸, C^{8'}), 126.53 (C⁶, C^{6'}), 127.83 (C⁷, C^{7'}), 128.46 (C⁵, C^{5'}), 130.42 (C², C^{2'}), 131.16 (C^{8a}, C^{8a'}), 132.47 (C⁴, C^{4'}), 133.85 (C^{4a}, C^{4a'}), 137.14 (C¹, C^{1'}), 199.74 (C⁹).

1,1'-Dinaphthyl thioketone (16)

Thioketone **16** was prepared from **15**, as previously described [9]. A single crystal of **16** was obtained from CH_2Cl_2 .

¹H-NMR δ (CDCl₃), ppm: 7.381 (td, ³*J* = 8.0 Hz, ³*J* = 7.5 Hz, 2H, H⁶, H^{6'}), 7.422 (td, ³*J* = 8.0 Hz, ³*J* = 7.5 Hz, 2H, H³, H^{3'}), 7.484 (td, ³*J* = 8.0 Hz, ³*J* = 7.0 Hz, 2H, H⁷, H^{7'}), 7.688 (dd, ³*J* = 7.0 Hz, 2H, H², H^{2'}), 7.880 (d, ³*J* = 8.0 Hz, 2H, H⁵, H^{5'}), 7.969 (d, ³*J* = 8.0 Hz, 2H, H⁴, H^{4'}), 8.222 (d, ³*J* = 8.5 Hz, 2H, H⁸, H^{8'}).

¹³C-NMR δ(CDCl₃), ppm: 124.79 (C³, C^{3'}), 125.77 (C⁸, C^{8'}), 126.28 (C⁶, C^{6'}), 127.34 (C⁷, C^{7'}), 127.99 (C², C^{2'}), 128.34 (C⁵, C^{5'}), 130.02 (C^{8a}, C^{8a'}), 131.68 (C⁴, C^{4'}), 133.98 (C^{4a}, C^{4a'}), 148.57 (C¹, C^{1'}), 241.58 (C⁹).

Di(1-naphthyl)hydrazone methanone (25)

Hydrazone **25** was prepared from **16**, as previously described [9].

¹H-NMR δ (CDCl₃), ppm: 5.589 (s, 2H), 7.215 (dd, ³J = 7.5 Hz, ⁴J = 1.5 Hz, 1H), 7.281 (t, ³J = 7.0 Hz, 1H) 7.753 (dd, ³J = 7.0 Hz, ³J = 1.0 Hz, 1H), 7.522–7.588 (m, 2H), 7.594 (t, ³J = 8.0 Hz, ³J = 7.5 Hz, 3H), 7.786 (d, ³J = 8.0 Hz, 1H), 7.895 (d, ³J = 7.5 Hz, 1H), 7.918 (d, ³J = 8.0 Hz, 1H), 7.975 (t, ³J = 9.0 Hz, ⁴J = 2.0 Hz, ⁴J = 1.6 Hz, 2H), 9.058 (d, ³J = 8.0 Hz, 1H).

	15	16	18	19
Empirical formula	C ₂₁ H ₁₄ O	$C_{21}H_{14}S$	C ₂₁ H ₁₄ O	C ₂₁ H ₁₄ O
Formula weight	282.32	298.38	282.32	282.32
Temperature (K)	295(1)	295(1)	173(1)	173(1)
Crystal system	Orthorhombic	Monoclinic	Monoclinic	Monoclinic
Space group	Pbcn	$P2_1/n$	P2 ₁	C2/c
a (Å)	10.8530(8)	12.2044(8)	8.336(1)	31.416(5)
<i>b</i> (Å)	12.1389(9)	7.3744(5)	6.0093(9)	6.1050(9)
<i>c</i> (Å)	33.894(2)	17.632(1)	17.784(2)	7.388(1)
α (°)	90	90	90	90
β (°)	90	105.257(1)	103.198(3)	96.986(3)
γ (°)	90	90	90	90
Volume (Å ³)	4465.3(6)	1530.9(2)	721.0(2)	1406.4(4)
Z	12	4	2	4
Density (calculated) (Mg/m ³)	1.260	1.295	1.300	1.333
Absorption coefficient (mm ⁻¹)	0.076	0.204	0.078	0.080
<i>F</i> (000)	1,776	624	296	592
Crystal size (mm ³)	$0.23\times0.21\times0.14$	$0.22\times0.20\times0.14$	$0.27\times0.23\times0.24$	$0.23 \times 0.20 \times 0.05$
Crystal color and shape	colorless plates	blue plates	colorless plates	pale brown plates
θ range for data collection (°)	2.23-27.99	1.83-28.00	2.51-26.99	2.61-27.98
Reflections collected	49,412	17,254	8,061	7,695
Independent reflections	5,325 [$R_{\rm int} = 0.0861$]	$3,644 \ [R_{\rm int} = 0.0316]$	$3,137 \ [R_{\rm int} = 0.0432]$	1,668 [$R_{int} = 0.0377$]
Absorption correction	None	None	None	None
Data/restraints/parameters	5325/0/299	3644/0/199	3137/1/199	1668/0/101
Goodness-of-fit on F^2	1.034	1.036	1.044	1.168
Final <i>R</i> indices $[I > 2\sigma_I]$	$R_1 = 0.0709$	$R_1 = 0.0593$	$R_1 = 0.0580$	$R_1 = 0.0763$
	$wR_2 = 0.1191$	$wR_2 = 0.1484$	$wR_2 = 0.1103$	$wR_2 = 0.1667$
R indices (all data)	$R_1 = 0.1647$	$R_1 = 0.0878$	$R_1 = 0.0775$	$R_1 = 0.0960$
	$wR_2 = 0.1508$	$wR_2 = 0.1650$	$wR_2 = 0.1169$	$wR_2 = 0.1783$

 Table 1
 Crystallographic data for dinaphthyl ketones 15, 18, and 19 and for thioketone 16

¹³C-NMR δ(CDCl₃), ppm: 124.84 (C–H), 125.58 (C–H), 125.74 (C–H), 126.02 (C–H), 126.57 (C–H), 126.58 (C–H), 126.63 (C–H), 126.97 (C–H), 127.27 (C–H), 127.70 (C–H), 128.32 (C–H), 128.69 (C–H), 128.73 (C–H), 129.28 (C–H), 130.10 (C), 131.19 (C), 132.83 (C), 133.95 (C), 134.39 (C), 136.05 (C), 148.29 (C).

1,1'-(Diazomethylene)bisnaphthylene (17)

It was prepared from **25**, as previously described [9]. IR: $v = 2,035 \text{ cm}^{-1}$.

¹H-NMR δ (CDCl₃), ppm: 7.355 (dd, ³*J* = 7.0 Hz, ⁴*J* = 1.5 Hz, 2H, H², H^{2'}), 7.393 (td, ³*J* = 7.5 Hz, ³*J* = 7.0 Hz, ⁴*J* = 1.5 Hz, 2H, H⁷, H^{7'}), 7.420 (td, ³*J* = 9.0 Hz, ³*J* = 7.0 Hz, ⁴*J* = 1.5 Hz, 2H, H³, H^{3'}), 7.497 (td, ³*J* = 8.0 Hz ³*J* = 7.5 Hz, ⁴*J* = 1.5 Hz, 2H, H⁶, H^{6'}), 7.779 (dd, ³*J* = 8.0 Hz, ⁴*J* = 1.5 Hz, 2H, H⁴, H^{4'}), 7.875 (dd, ³*J* = 7.5 Hz, ⁴*J* = 1.0 Hz, 2H, H⁸, H^{8'}), 7.892 (dd, ³*J* = 7.0 Hz, ⁴*J* = 1.0 Hz, 2H, H⁵, H^{5'}).

¹³C-NMR δ(CDCl₃), ppm: 58.31 (C=N), 124.78 (C⁸, C⁸), 125.81 (C³, C³), 126.12 (C⁶, C^{6'}), 126.33 (C⁷, C^{7'}), 126.39 (C², C^{2'}), 127.74 (C⁴, C^{4'}), 128.67 (C¹, C^{1'}), 128.93 (C⁵, C^{5'}), 130.53 (C^{8a}, C^{8a'}), 134.50 (C^{4a}, C^{4a'}).

2-Naphthalenecarbonyl chloride (26)

2-Naphthanoic acid (Acros, 2 g, 11.6 mmol) was dissolved in freshly distilled $SOCl_2$ (15 mL) in a roundbottomed flask equipped with a magnetic stirrer and under argon. The reaction mixture was refluxed for 2 h, then cooled to RT and evaporated under reduced pressure to give **26** as an oily compound, 2.13 g, yield 96%.

¹H-NMR δ (CDCl₃), ppm: 7.599 (t, ³*J* = 7.2 Hz, 1H), 7.673 (t, ³*J* = 7.2 Hz, ³*J* = 6.8 Hz, 1H), 7.866–7.894 (m, 2H), 7.974 (d, ³*J* = 8.4 Hz, 1H), 8.023 (dd, ³*J* = 8.8 Hz, 1H), 8.656 (s, 1H).

1-Naphthyl-2'-naphthyl ketone (18)

Ketone 18 was prepared according to a literature procedure with some modifications [16]. Compound 26 (5 g, 26.2 mmol) was added to a stirred solution of anhydrous AlCl₃ (3.5 g, 26.2 mmol) in dry CH₂Cl₂ (50 mL). The reaction mixture was stirred for 5 min, then cooled to 0 °C and naphthalene in one portion (3.35 g, 26.2 mmol) was added. The color turned deep red. After stirring for 2 h, the reaction mixture was poured on the mixture of ice and HCl, extracted with CH₂Cl₂, washed with an aqueous solution of NaHCO₃, dried on MgSO₄, filtered, and evaporated under reduced pressure. The brown crude product was purified by column chromatography on silica gel; the crude product was dissolved in CHCl₃, evaporated on silica gel, and eluted with PE/CH₂Cl₂ 98:2. The target product 18 was isolated and obtained as a yellow powder, 3.60 g, yield 49%, mp 134 °C (lit. [17] 135–136 °C). A single crystal of 18 was obtained from CH₂Cl₂.

¹H-NMR δ (CDCl₃), ppm: 7.492–7.536 (m, 2H, H⁷, H^{7'}), 7.558 (2t, ³*J* = 7.5 Hz, 2H, H³, H⁶), 7.615 (td, ³*J* = 7.5 Hz, 1H, H^{6'}), 7.657 (dd, ³*J* = 7.5 Hz, 1H, H²), 7.833 (d, ³*J* = 8.5 Hz, 1H, H^{8'}), 7.911 (d, ³*J* = 8.0 Hz, 1H, H^{5'}), 7.948 (d, ³*J* = 8.5 Hz, 1H, H^{4'}), 7.963 (d, ³*J* = 6.5 Hz, 1H, H⁵), 8.052 (d, ³*J* = 8.5 Hz, 1H, H⁴), 8.095 (dd, ³*J* = 8.7 Hz, 1H, H^{3'}), 8.136 (d, ³*J* = 9.0 Hz, 1H, H⁸), 8.264 (s, 1H, H^{1'}).

¹³C-NMR δ (CDCl₃), ppm: 124.39 (C³), 125.36 (C^{3'}), 125.74 (C⁸), 126.47 (C⁶), 126.76 (C^{7'}), 127.24 (C⁷), 127.65 (C²), 127.79 (C^{5'}), 128.40 (C^{4'}), 128.41 (C⁵), 128.63 (C^{6'}), 129.65 (C^{8'}), 131.06 (C^{8a}), 131.17 (C⁴), 132.37 (C^{8a'}), 132.84 (C^{1'}), 133.77 (C¹), 135.68 (C^{4a'}), 135.70 (C^{2'}), 136.56 (C^{4a}), 197.95 (C⁹).

1-Naphthyl-2'-naphthyl thioketone (20)

In a round-bottomed flask equipped with reflux condenser protected with CaCl₂ tube and a magnetic stirrer, ketone **18** (2.50 g, 8.80 mmol) was dissolved in dry toluene (40). Lawesson's reagent (LR) (Acros) (1.79 g, 4.40 mmol) was added. The reaction mixture was stirred with reflux for 4 h. The color of the reaction mixture turned from yellow to green. After cooling to RT, the solvent was evaporated under reduced pressure. The crude product was purified by column chromatography on dry silica gel; the product was dissolved in benzene and eluted with PE/CH₂Cl₂ 95:5. The first fraction was collected and evaporated. A blue powder of the **20** was obtained, 1.95 g, yield 74%, mp 104 °C.

¹H-NMR δ (CDCl₃), ppm: 7.318 (td, 1H, H⁷), 7.449 (td, ³*J* = 7.5 Hz, 1H, H^{7'}), 7.456 (td, ³*J* = 7.5 Hz, 1H, H⁶), 7.558 (t, ³*J* = 6.5 Hz, 1H, H³), 7.569–7.602 (m, 2H, H², H^{6'}), 7.691 (d, ³*J* = 8.5 Hz, 1H, H⁸), 7.759 (d, ³*J* = 8.0 Hz, 1H, H^{8'}), 7.811 (d, ³*J* = 9.0 Hz, 1H, H^{4'}), 7.835 (d,

 ${}^{3}J = 8.0$ Hz, 1H, H^{5'}), 7.914 (d, ${}^{3}J = 8.5$ Hz, 1H, H⁵), 7.978 (d, ${}^{3}J = 7.5$ Hz, 1H, H⁴), 8.154 (s, 1H, H^{1'}), 8.190 (dd, ${}^{3}J = 9.0$ Hz, 1H, H^{3'}).

¹³C-NMR δ (CDCl₃), ppm: 125.04 (C³), 125.50 (C^{3'}), 126.02 (C²), 126.14 (C⁶, C⁸), 126.61 (C⁷), 126.90 (C^{7'}), 127.77 (C^{5'}), 128.20 (C⁵), 128.30 (C^{4'}), 128.90 (C^{6'}), 129.60 (C⁴), 130.05 (C^{8a'}), 130.27 (C^{1'}), 130.37 (C^{8'}), 132.53 (C^{8a'}), 133.50 (C^{4a}), 135.59 (C^{4a'}), 143.45 (C^{2'}), 147.52 (C¹), 239.41 (C⁹).

Di-1,2-naphthlenylmethanone hydrazone (27)

To thioketone **20** (3.9 g, 13.17 mmol) dissolved in ethanol (28 mL), benzene (12 mL) and hydrazine hydrate (Fluka) (3.1 mL, 64.32 mmol) were added. The blue color of the solution changed immediately to yellow. The reaction mixture was refluxed for 2 h. The solvent was evaporated under reduced pressure, the crude product treated several times with ethanol and the solvent evaporated. A yellow powder of **27** was obtained, 3.2 g, yield 83%, mp 135–137 °C.

¹H-NMR δ (CDCl₃), ppm: 5.483 (s, 2H), 7.356 (td, ³*J* = 8.5 Hz, ⁴*J* = 1.5 Hz, 1H), 7.411 (td, ³*J* = 7.5 Hz, ³*J* = 7.0 Hz, ⁴*J* = 1.5 Hz, 1H), 7.435 (dd, ³*J* = 8.0 Hz, ⁴*J* = 1.5 Hz, 1H), 7.473 (dd, ³*J* = 7.0 Hz, ⁴*J* = 1.0 Hz, 1H), 7.486 (s, 1H), 7.573 (dd, ³*J* = 8.5 Hz, ³*J* = 8.0 Hz, ⁴*J* = 1.0 Hz, 1H), 7.574 (d, ³*J* = 8.5 Hz, 1H), 7.665 (td, ³*J* = 8.5 Hz, ³*J* = 7.5 Hz, ⁴*J* = 1.5 Hz, 1H), 7.707 (d, ³*J* = 8.0 Hz, 1H), 7.793 (d, ³*J* = 8.5 Hz, 1H), 7.825 (d, ³*J* = 8.5 Hz, 1H), 7.982 (d, ³*J* = 8.5 Hz, 1H), 8.022 (d, ³*J* = 8.5 Hz, 1H), 8.119 (dd, ³*J* = 8.5 Hz, ⁴*J* = 1.5 Hz, 1H).

¹³C-NMR δ(CDCl₃), ppm: 123.39 (C–H), 125.42 (C–H), 126.03 (C–H), 126.05 (C–H), 126.09 (C–H), 126.26 (C–H), 126.71 (C–H), 127.15 (C–H), 127.18 (C–H), 127.58 (C–H), 127.94 (C–H), 128.35 (C–H), 128.66 (C–H), 129.40 (C–H), 130.47 (C), 131.11 (C), 133.25 (C), 133.33 (C), 134.04 (C), 136.13 (C), 147.97 (C).

1,2-(Diazomethylene)bisnaphthylene (22)

To a stirred solution of hydrazone **27** (2.94 g, 10.0 mmol) in Et₂O (60 mL) protected by CaCl₂ tube, anhydrous Na₂SO₄ (4.79 g, 34.0 mmol) was added. The reaction mixture was cooled to 0 °C, then freshly prepared saturated solution of KOH (Acros, pellets) in ethanol (4 mL), and yellow HgO (14.8 g, 69.0 mmol) were added. The color of the solution changed gradually from yellow to red. After 3 h of stirring at 0 °C the reaction was complete. After filtration the residue was washed with dry Et₂O. The combined organic fractions were evaporated under reduced presser to give 2.5 g of 22 as a red powder, yield 96%, mp 118–120 °C.

IR: $v = 2,036 \text{ cm}^{-1}$.

¹H-NMR δ (CDCl₃), ppm: 7.225 (dd, ³*J* = 9.0 Hz, ⁴*J* = 2.0 Hz, 1H, H^{3'}), 7.354 (s, 1H, H^{1'}), 7.402 (td, ³*J* = 7.5 Hz, ³*J* = 7.0 Hz, ⁴*J* = 1.5 Hz, ⁴*J* = 1.0 Hz 1H, H^{6'}), 7.438 (td, ³*J* = 8.0 Hz, ³*J* = 6.0 Hz, ⁴*J* = 1.5 Hz, 1H, H^{7'}), 7.504 (td, ³*J* = 8.0 Hz, ³*J* = 7.5 Hz, ⁴*J* = 1.5 Hz, 1H, H⁷), 7.576 (td, ³*J* = 8.0 Hz, ³*J* = 7.5 Hz, ⁴*J* = 1.0 Hz, 1H, H⁶), 7.625 (d, ³*J* = 8.5 Hz, 1H, H^{8'}) 7.635 (t, 1H, H³), 7.785 (dd, ³*J* = 7.5 Hz, ⁴*J* = 1.0 Hz, 1H, H²), 7.806 (d, 1H, ³*J* = 7.0 Hz, H^{5'}), 7.822 (d, 1H, ³*J* = 9.0 Hz, H^{4'}), 7.963 (d, ³*J* = 8.5 Hz, 1H, H⁸), 7.995 (2d, ³*J* = 8.5 Hz, 2H, H⁴, H⁵).

¹³C-NMR δ (CDCl₃), ppm: 59.88 (C=N), 120.06 (C^{1'}), 121.53 (C^{3'}), 124.86 (C^{6'}), 125.28 (C⁸), 125.46 (C¹), 125.92 (C³), 126.36 (C⁶), 126.53 (C^{7'}), 126.75 (C⁷), 126.98 (C^{8'}), 127.67 (C^{5'}), 128.74 (C^{4'}), 128.78 (C⁵), 129.16 (C^{2'}), 129.26 (C⁴), 129.41 (C²), 130.84 (C^{4a'}), 132.07 (C^{8a}), 133.98 (C^{8a'}), 134.37 (C^{4a}).

2,2'-Dinaphthyl ketone (19)

Ketone 19 was prepared according to a literature procedure with some modifications [18]. A solution of 2-bromonaphthalene (Merck) (1.2 g, 5.79 mmol) in ether (10 mL) under argon was added dropwise to Mg (Acros) (0.97 g, 40.59 mmol) in ether (15 mL) with 2-3 drops of 1,2dibromoethane and then heated gradually to 60 °C while benzene (15 mL) and ether (27 mL) were added. After 1 h the reaction mixture was decanted to a round-bottomed three-necked flask. 2-Naphthalenecarbonyl chloride 26 (2.20 g, 11.59 mmol) was dissolved in Et₂O (5 mL) and added dropwise while cooling the reaction flask in ice bath. The reaction mixture was stirred at 0 °C for 10 min, at RT for 10 min and then warmed gradually to 80 °C and refluxed for 1 h. The reaction mixture was quenched with saturated NH₄Cl solution, extracted with Et₂O, dried on MgSO₄, filtered, and the solvent evaporated under reduced pressure. The brown crude product was purified by column chromatography on silica gel; the crude product was dissolved in CHCl₃ and evaporated on silica gel, eluted with PE/CH₂Cl₂ 98:2. Ketone 19 was isolated as a yellow powder, 3.60 g, yield 49%, mp 166 °C (lit. [17] 164-165 °C, lit. [18] 163-164 °C). A single crystal of 19 was obtained from EtOAc.

¹H-NMR δ (CDCl₃), ppm: 7.571 (td, ³*J* = 7.5 Hz, 2H, H⁷, H⁷), 7.635 (td, ³*J* = 8.5 Hz, 2H, H⁶, H^{6'}), 7.931 (d, ³*J* = 7.0 Hz, 2H, H⁸, H^{8'}), 7.945 (d, ³*J* = 7.5 Hz, 2H, H⁵, H^{5'}), 7.993–8.00 (m, 4H, H³, H^{3'}, H⁴, H^{4'}), 8.330 (s, 2H, H¹, H^{1'}).

¹³C-NMR δ(CDCl₃), ppm: 125.88 (C³, C^{3'}), 126.83 (C⁷, C^{7'}), 127.85 (C⁵, C^{5'}), 128.31 (C⁶, C^{6'}), 128.35 (C⁴, C^{4'}),

129.43 (C⁸, C^{8'}), 131.82 (C¹, C^{1'}), 132.30 (C^{8a}, C^{8a'}), 135.17 (C^{4a}, C^{4a'}), 135.27 (C², C^{2'}), 196.82 (C⁹).

2,2'-Dinaphthyl thioketone (21)

In a round-bottomed flask equipped with reflux condenser protected with $CaCl_2$ tube and a magnetic stirrer, ketone **19** (0.5 g, 1.7 mmol) was dissolved in benzene (30 mL). LR [19] (Acros) (0.35 g, 0.88 mmol) was added. The reaction mixture was stirred with reflux for 4 h. The color of the reaction mixture turned from yellow to greenish-blue. After cooling to RT, the solvent was evaporated almost to dryness and the crude product was purified by column chromatography on dry silica gel using PE/CH₂Cl₂ 95:5 as eluent. The first fraction was collected and evaporated under reduced pressure. Blue crystals of **21** were obtained 0.21 g, yield 41%, mp 136 °C.

¹H-NMR δ (CDCl₃), ppm: 7.532 (td, ³*J* = 7.5 Hz, 2H, H⁷, H^{7'}), 7.613 (td, ³*J* = 8.0 Hz, ³*J* = 7.5 Hz, 2H, H⁶, H^{6'}), 7.873 (d, ³*J* = 8.5 Hz, 2H, H⁴, H^{4'}), 7.889 (d, ³*J* = 7.0 Hz, 2H, H⁸, H^{8'}), 7.899 (d, ³*J* = 7.5 Hz, 2H, H⁵, H^{5'}), 7.991 (dd, ³*J* = 8.5 Hz, 2H, H³, H^{3'}), 8.184 (s, 2H, H¹, H^{1'}).

¹³C-NMR δ(CDCl₃), ppm: 126.96 (C⁷, C^{7'}), 127.15 (C³, C^{3'}), 127.79 (C⁵, C^{5'}), 127.83 (C⁴, C^{4'}), 128.26 (C⁶, C^{6'}), 129.77 (C⁸, C^{8'}), 129.96 (C¹, C^{1'}), 132.31 (C^{8a}, C^{8a'}), 135.05 (C^{4a}, C^{4a'}), 144.91 (C², C^{2'}), 237.31 (C⁹).

Di-2-naphthlenylmethanone hydrazone (28)

Thioketone **21** (0.2 g, 0.67 mmol) was dissolved in ethanol (12 mL); benzene (8 mL) and hydrazine hydrate (Fluka) (0.16 mL, 3.35 mmol) were added. The blue color of the solution changed immediately to yellow. The reaction mixture was refluxed for 2 h. The solvent was evaporated under reduced pressure, the crude product treated several times with ethanol and the solvent evaporated. A yellow powder of **28** was obtained, 0.17 g, yield 85%, mp 135–136 °C (lit. [20] 138–141 °C).

¹H-NMR δ (CDCl₃), ppm: 5.574 (s, 2H), 7.388 (td, ³J = 7.5 Hz, ⁴J = 1.5 Hz, 1H), 7.410 (dd, ³J = 7.0 Hz, ⁴J = 1.5 Hz, 1H), 7.439 (dd, ³J = 8.5 Hz, ⁴J = 1.5 Hz, 1H), 7.560 (s, 1H), 7.584 (td, ³J = 8.5 Hz, 1H), 7.603 (td, ³J = 7.5 Hz, ⁴J = 1.5 Hz, 1H), 7.637 (dd, ³J = 8.0 Hz, ⁴J = 1.0 Hz, 1H), 7.809 (d, ³J = 8.0 Hz, 1H), 7.819 (d, ³J = 8.5 Hz, 1H), 7.887 (s, 1H), 7.914 (d, ³J = 8.0 Hz, 1H), 7.962 (d, ³J = 8.0 Hz, 1H), 8.049 (d, ³J = 8.5 Hz, 1H), 8.053 (d, ³J = 9.0 Hz, 1H).

¹³C-NMR δ(CDCl₃), ppm: 123.73 (C–H), 126.08 (C–H), 126.11 (C–H), 126.29 (C–H), 126.67 (2(C–H)), 126.93 (C–H), 127.53 (C–H), 127.86 (C–H), 127.95 (C–H), 128.27

(C-H), 128.32 (C-H), 128.49 (C-H), 129.42 (C-H), 130.38 (C), 133.16 (C), 133.30 (C), 133.38 (C), 133.58 (C), 136.09 (C), 149.10 (C).

2,2'-(Diazomethylene)bisnaphthylene (23)

To a stirred solution of hydrazone **28** (0.35 g, 1.18 mmol) in Et₂O (15 mL) protected by CaCl₂ tube, anhydrous Na₂SO₄ (0.56 g, 4.02 mmol) was added. The reaction mixture was cooled to 0 °C, then freshly prepared saturated solution of KOH (Acros, pellets) in ethanol (1 mL), and yellow HgO (1.76 g, 8.15 mmol) were added. The color of the solution changed gradually from yellow to red. After 3 h of stirring at 0 °C the reaction was complete. After filtration the residue was washed with dry Et₂O. The combined organic fractions were evaporated under reduced presser to give **23**, 0.341 g, as a red powder, yield 98%, mp 121–122 °C (lit. [20] 125.8–127.3 °C).

IR: $v = 2,038 \text{ cm}^{-1}$

¹H-NMR δ (CDCl₃), ppm: 7.437–7.478 (m, 4H, H³, H^{3'}, H⁶, H^{6'}), 7.487 (td, ³*J* = 7.5 Hz, ⁴*J* = 1.5 Hz, ⁴*J* = 1.0 Hz, 2H, H⁷, H^{7'}), 7.758 (d, ³*J* = 7.5 Hz, 2H, H⁸, H^{8'}), 7.497 (s, 2H, H¹, H^{1'}), 7.837 (d, ³*J* = 8.0 Hz, 2H, H⁵, H^{5'}), 7.892 (d, ³*J* = 8.5 Hz, 2H, H⁴, H^{4'}).

¹³C-NMR δ (CDCl₃), ppm: 58.39 (C=N), 123.37 (C¹, C^{1'}), 123.69 (C³, C^{3'}), 125.61 (C⁶, C^{6'}), 126.64 (C⁷, C^{7'}), 126.96 (C², C^{2'}), 127.31 (C⁸, C^{8'}), 127.73 (C⁵, C^{5'}), 128.92 (C⁴, C^{4'}), 131.73 (C^{4a}, C^{4a'}), 133.91 (C^{8a}, C^{8a'}).

Method of calculations

The quantum mechanical calculations were performed using the Gaussian03 [21] package. Becke's threeparameter hybrid density functional B3LYP [22], with the non-local correlation functional of Lee et al. [23] was used. The split valence 6-31G(d) basis set was employed. All structures were fully optimized using the symmetry constraints as indicated. Vibrational frequencies were calculated to verify the nature of the stationary points. Non-scaled thermal corrections to Gibbs' free energy were used.

Results and discussion

Synthesis

according to a literature procedure [16] with some modifications. The low temperature favored the acylation at the 1-position of naphthalene, yielding the kinetically controlled product 18 but not the thermodynamically controlled 19. Ketone 19 was prepared by a Grignard reaction of 2-naphthylmagnesium bromide and 2-naphthalenecarbonyl chloride (26) according to a literature procedure [18] with some modifications. Thioketones 20 and 21 were prepared by a reaction of the corresponding ketones 18 and 19 with LR [19]. The diazomethane derivatives 22 and 23 were prepared by reactions the thicketones 20 and 21 with hydrazine hydrate to give the hydrazones 27 and 28, respectively, followed by oxidation of the hydrazones with HgO/KOH/Na₂SO₄. All the structures were verified by ¹H-NMR and ¹³C-NMR spectroscopy. Only one diastereomer of hydrazone 27, with E-configuration of the C=N bond, was formed. Its stereochemistry was assigned on the basis of a comparison of the H⁸ chemical shifts in the ¹H-NMR spectra of the hydrazones of the three dinaphthyl ketones. In hydrazone 25, the derivative of 1,1'-dinaphthyl ketone (15), H^8 is considerably deshielded appearing at $\delta =$ 9.06 ppm. By contrast, the corresponding H^8 in the hydrazones 27 and 28, the derivatives of 1,2'-dinaphthyl ketone (18) and of 2,2'-dinaphthyl ketone (19), respectively, appear in the aromatic region at $\delta < 8.2$ ppm. Thus, H⁸ of 1-naphthyl moiety is in proximity to the N=NH₂ functional group only in 25. The diazomethanes 17, 22, and 23 showed the characteristic IR absorptions at ca. $2,035 \text{ cm}^{-1}$. Scheme 1 describes the synthesis of the 1,1'-dinaphthyl derivatives 15, 16, and 17. Scheme 2 describes the synthesis of the 1,2'-dinaphthyl derivatives 18, 20, and 22. Scheme 3 describes the synthesis of the 2,2'-dinaphthyl derivatives 19, 21, and 23.

Molecular and crystal structure

The crystallographic data for the three dinaphthyl ketones **15**, **18**, and **19** and for the thioketone **16** are given in Table 1 (CCDC-711659, 711660, 835295 and 835296 contain the supplementary crystallographic data for compounds **15**, **16**, **18** and **19**. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0)1223-336033; email: deposit@ccdc.cam.ac.uk]). The ORTEP diagrams of **15**, **16**, **18**, and **19** as determined by X-ray crystallography are presented in Figs. 2, 3, 4, and **5**. Ketone **15** crystallizes in the orthorhombic space group *Pbcn*. Ketones **18** and **19** and thioketone **16** crystallize in the monoclinic space groups $P2_1$, C2/c, and $P2_1/n$, respectively.

Scheme 1 Synthesis of the 1,1'-dinaphthyl derivatives 15, 16, and 17





Scheme 2 Synthesis of the 1,2'-dinaphthyl derivatives 18, 20, and 22



Scheme 3 Synthesis of the 2,2'-dinaphthyl derivatives 19, 21, and 23

Table 2 gives selected geometrical parameters derived from the crystal structures of 15, 16, 18, and 19 and from the DFT study (vide infra). The following geometrical parameters were considered: the twist angles τ_1 and τ_2 around the naphthyl–carbonyl bond; the bond angle β at the C^9 carbon atom; the dihedral angle θ between the leastsquare planes of the naphthyl systems; the pyramidalization angles χ at C¹, C², and C⁹. The unit cell of **15** contains 12 molecules of two crystallographic conformations 15a and 15b. Conformation 15b contains a C₂-axis passing through the carbonyl group. The conformations 15a and 15b differ in their dihedral angles between the two naphthyl group, $\theta = 84.0^{\circ}$ and 77.9°, respectively, and in the twist angles of the carbonyl group relative to the naphthyl groups: $\tau_1(O^{10}-C^9-C^1-C^{8a}) = -36.5^\circ$ and $\tau_1(O^{10}-C^9-C^{1'})$ $-C^{8a'}$ = -46.7° in **15a** and $\tau_1(O^{10''}-C^{9''}-C^{1''}-C^{8a''}) =$ -37.1° in **15b**. The thiocarbonyl group of **16** is significantly more twisted than the carbonyl group of **15a**: $\tau_1(S^{10}-C^9-C^1-C^{8a}) = -40.3^\circ$ and $\tau_2(S^{10}-C^9-C^{12})$ $-C^{8a'}$ = -54.3°. The folding angle between the naphthyl groups of 16 is nearly orthogonal, $\theta = 88.7^{\circ}$. The deviations from planarity of the carbonyl groups of 15a, 15b, and of the thiocarbonyl group of 16 are probably due to the short non-bonding distances between the peri-hydrogens H⁸...H^{8'} in the respective (hypothetical) planar conformations. Several non-bonding distances in 15 and 16 are shorter than the sum of the respective van der Waals radii of hydrogen (115 ppm), oxygen (129 ppm), carbon (171 ppm), and sulfur (184 ppm) [24]. They are $C^9 \cdots H^2 = 257.2 \text{ pm}$ and $C^9 \cdots H^{2^7} = 257.8 \text{ pm}$ (15a, 10%) penetration); $C^{9''} \cdots H^{2''} = 260.3$ (**15b**, 9% penetration); $C^{9''} \cdots H^{8''} = 266.0$ (15b, 7% penetration); $C^9 \cdots H^2 = 260.9$ (16, 9% penetration); $C^9 \cdots H^{2'} = 255.3$ (16, 11% penetration); $C^9 \cdots H^8 = 265.3$ (16, 7% penetration).



Fig. 2 ORTEP drawing of 1,1'-dinaphthyl ketone (15a, left; 15b, right), scaled to enclose 50% probability



In 2,2'-dinaphthyl ketone (19), the twist angles of the carbonyl group relative to the naphthyl groups are significantly smaller, than in 15a and 15b: $\tau_1(O^{10}-C^9-C^2-C^1) = -25.0^\circ$, indicating less overcrowding in the former. Indeed, the only short non-bonding distance in 19 is $C^9 \cdots H^1 = 259.3$ pm (9% penetration) Nevertheless, the non-negligible deviation from planarity in 19 (the naphthyl folding angle $\theta = 51.0^\circ$), in spite of the 2,2'-substitution pattern, is noted. In 1,2-substituted ketone 18, the twist angles of the two naphthyl groups relative to the C=O bond differ sharply: $\tau_2(C^{10}-C^9-C^1-C^{8a}) = 51.6^\circ$



Fig. 3 ORTEP drawing of 1,1'-dinaphthyl thioketone (16), scaled to enclose 50% probability



Fig. 4 ORTEP drawing of 1,2'-dinaphthyl ketone (18), scaled to enclose 50% probability

versus $\tau_2(O^{10}-C^9-C^{2'}-C^{1'}) = 21.1^\circ$, highlighting the effect of the site of substitution (1 vs. 2). Ketone **18**, like **15** and **16**, is overcrowded with the short non-bonding distances of $C^9 \cdots H^2 = 257.0 \text{ pm}, C^9 \cdots H^{1'} = 264.0 \text{ pm}, \text{ and } C^9 \cdots H^{3'} = 266.1 \text{ pm}.$





Table 2 Selected geometrical parameters of the X-ray molecular structures and of the respective DFT calculated structures of 15, 16, 18, and 19

X	Conform	nations		$\tau_1{}^a$ (°)	τ_2^{b} (°)	β^{c} (°)	$\chi(C^9)^d$ (°)	$\chi(C^1)/\chi(C^2)^d$ (°)	$\theta^{\rm e}$ (°)	X ¹⁰ –C ⁹ (pm)	C^9-C^1/C^2 $C^9-C^{1'}/C^{2'}$ (pm)
0	X-ray	15a	C_1	-36.5	139.1	117.6	-0.5	4.4	84.0	121.9	148.9
				-46.7	127.8			5.6			149.9
		15b	C_2	-37.1	137.6	119.4	0.0	5.2	77.9	121.8	149.3
0	1Z, 1'Z	15	C_2	-34.4	141.1	118.5	0.0	4.5	67.6	122.8	150.4
S	X-ray	16	C_1	-40.3	134.2	117.1	-8.0	5.5	88.7	162.6	148.8
				126.4	-54.3			0.7			149.2
S	1Z, 1'E	16	C_1	-45.4	131.3	117.2	6.1	3.3	83.6	165.8	148.7
				132.5	-47.3			-0.1			149.1
0	X-ray	18	C_1	-127.0	51.6	120.8	3.6	1.4	72.1	122.7	150.1
				-154.5	21.1			4.4			148.4
0	1E,2'E	18	C_1	-125.0	52.2	120.5	4.0	2.8	68.1	122.5	151.0
				-161.7	14.5			3.8			149.7
0	X-ray	19		-25.0	151.4	120.6	0.0	3.7	51.0	120.9	150.0
0	2Z,2'Z	19	C_2	-26.8	149.9	120.3	0.0	3.4	51.1	122.7	150.1

^a For **15** and **16**, $X^{10}-C^9-C^1-C^{8a}$ and $X^{10}-C^9-C^{1'}-C^{8a'}$ torsion angles; for **18**, $X^{10}-C^9-C^1-C^{8a}$ and $X^{10}-C^9-C^{2'}-C^{1'}$ torsion angles; for **19**, $X^{10}-C^9-C^2-C^1$ and $X^{10}-C^9-C^{2'}-C^{1'}$ torsion angles

^b For **15** and **16**, $X^{10}-C^9-C^1-C^2$ and $X^{10}-C^9-C^{1'}-C^{2'}$ torsion angles; for **18**, $X^{10}-C^9-C^1-C^2$ and $X^{10}-C^9-C^{2'}-C^{3'}$ torsion angles; for **19**, $X^{10}-C^9-C^2-C^3$ and $X^{10}-C^9-C^2-C^{3'}$ torsion angles

^c For 15 and 16, $C^1-C^9-C^{1'}$ bond angle; for 18, $C^1-C^9-C^{2'}$ bond angle; for 19, $C^2-C^9-C^{2'}$ bond angle

^d $\chi(C^9)$ —the improper torsion angle $C^1 - C^9 - X^{10} - C^{1'}/C^1 - C^9 - X^{10} - C^{2'}/C^2 - C^9 - X^{10} - C^{2'} - 180^\circ \pmod{360^\circ}$; $\chi(C^1)/\chi(C^2)$ —the improper torsion angles $C^{8a} - C^1 - C^9 - C^2$ and $C^1 - C^2 - C^9 - C^3$, respectively, $-180^\circ \pmod{360^\circ}$

^e The dihedral angle between the least-square planes of the carbon atoms of the naphthyl moieties

The most interesting feature in the molecular structures of **15**, **16**, **18**, and **19** is the variety of conformations in the solid state. Each dinaphthyl derivative may adopt four major conformations defined by the twist angles around the carbon–carbon bonds connecting C⁹ and the two naphthyl groups, e.g., 1Z,2'Z, 1Z,2'E, 1E,2'Z, and 1E,2'E for the 1,2'dinaphthyl derivatives. *E* and *Z* are stereodescriptors applied to the structures with fractional bond order of the bond, e.g., between the carbonyl carbon (C⁹) and the naphthalene carbons (C¹, C², C^{1'}, C^{2'}) [25]. Ketones **15** (**15a**, **15b**) and **19** adopt 1Z,1'Z- and 2Z,2'Z-conformations, respectively; ketone **18** adopts a 1E,2'E-conformation; thioketone **16** adopts a 1E,1'Z-conformation. Furthermore, in the homo-substituted 1,1'- and 2,2'-dinaphthyl ketones **15** and **19**, *Z*,*Z* is the preferred conformation, in contrast to the homo-substituted 1,1'-dinaphthyl thioketone (**16**) which prefers the *E*,*Z*-conformation. The hetero-substituted 1,2'-dinaphthyl ketone prefers the 1*E*,2'*E*-conformation. It is not unexpected that in the 1,1'-dinaphthyl derivative **15**, the 1*Z*,1'*Z*-conformation would be more stable than the 1*E*,1'*E*-and 1*E*,1'*Z*-conformations. The differences in stabilities probably stems from the unfavorable non-bonding *peri*-hydrogen interactions $H^8 \cdots H^8'$ and $H^8 \cdots H^{2'}$ in the 1*E*,1'*E*-and 1*E*,1'*Z*-conformations, respectively, as compared with the non-bonding *ortho*-hydrogens interaction $H^2 \cdots H^{2'}$ in the 1*Z*,1'*Z*-conformation. The 1*E*,2'*Z*-conformation of **16** is unexpected and may be ascribed to intermolecular interactions in the crystal. In the 2,2'-dinaphthyl derivative **19**,

there are only non-bonding ortho-hydrogens interactions and no non-bonding *peri*-hydrogen interactions: H³...H^{3'}, $H^1 \cdots H^{1'}$, and $H^1 \cdots H^{3'}$ in the 2Z,2'Z-, 2E,2'E-, and 2E,2'Zconformations, respectively. It appears that the non-bonding interactions of ortho-H¹ are less favored than those of ortho-H³, resulting in the preferred 1Z,1'Z-conformation of 19.

It should not be overlooked that the variety in the conformations is a consequence not only of the molecular structures but also of the intermolecular interactions dictated by the crystal structures.

NMR spectroscopy

¹H- and ¹³C-NMR spectroscopic studies of **15–23** were carried out. Complete assignments were made through 2-dimensional correlation spectroscopy (DQF-COSY, HSQC, and HMBC). Tables 3, 4, and 5 give the ¹H-NMR chemical shifts (δ (¹H), ppm) of the dinaphthyl ketones **15**, 18, and 19, of the dinaphthyl thicketones 16, 20, and 21, and of the dinaphthyl diazomethanes 17, 22, and 23, respectively. Tables 3, 4, and 5 also contain the corresponding $\Delta\delta(^{1}\text{H})$ values: $\Delta\delta((\text{NA})_{2}\text{C=O})$, $\Delta\delta((\text{NA})_{2}\text{C=S})$, and $\Delta\delta((NA)_2=CN_2)$, where $\Delta\delta((NA)_2C=O) = \delta(18)$ - $\delta(15)$ and $\delta(18) - \delta(19)$; $\Delta \delta((NA)_2 C = S) = \delta(20) - \delta(16)$ and $\delta(20) - \delta(21); \ \Delta \delta((NA)_2 C = N_2) = \delta(22) - \delta(17) \text{ and } \delta(22) - \delta(17)$ $\delta(23)$; NA = naphthyl. The $\Delta\delta$ values express the differences of chemical shifts between the 1,2'-dinaphthyl derivatives and the respective 1,1'-dinaphthyl and

Table 3 ¹H-NMR chemical shifts (δ (¹H), ppm) and chemical shift differences ($\Delta \delta$ (¹H), ppm) of the dinaphthyl ketones **15**, **18**, and **19**

	15 , $\delta({}^{1}\text{H})$	18 , δ(¹ H)	19 , δ(¹ H)	$\Delta\delta$ (¹ H)
H^1	-	_	8.330s	_
H^2	7.616dd	7.657dd	-	0.041 ^a
H^3	7.440t	7.558t	7.993-8.00m	0.118 ^a
H^4	8.033d	8.052d	7.993-8.00m	0.019 ^a
H^5	7.954ddd	7.963d	7.945d	0.009^{a}
H^6	7.575–7.600m	7.558t	7.635td	-0.030^{a}
H^7	7.575–7.600m	7.492–7.536m	7.571td	-0.074^{a}
H^8	8.576ddd	8.136d	7.931d	-0.440^{a}
$\mathrm{H}^{1'}$	-	8.264s	8.033s	0.231 ^b
$H^{2'}$	7.616dd	-	-	-
$\mathrm{H}^{3'}$	7.440t	8.095dd	7.993-8.000m	0.099 ^b
$\mathrm{H}^{4'}$	8.033d	7.948d	7.993-8.000m	-0.048^{b}
$\mathrm{H}^{5'}$	7.954ddd	7.911d	7.946d	-0.035^{b}
$\mathrm{H}^{6'}$	7.575–7.600m	7.615td	7.635td	-0.020^{b}
$\mathrm{H}^{7'}$	7.575–7.600m	7.492–7.536m	7.571td	-0.057^{b}
H ^{8′}	8.576ddd	7.833d	7.931d	-0.098^{b}

^a $\Delta\delta(18) - (15)(^{1}H)$

^b $\Delta\delta(18) - (19)(^{1}H)$

Table 4 ¹H-NMR chemical shifts (δ (¹H), ppm) and chemical shift differences ($\Delta \delta$ (¹H), ppm) of the dinaphthyl thicketones **16**, **20**, and 21

	16 , $\delta({}^{1}\text{H})$	20 , $\delta(^{1}\mathrm{H})$	21 , $\delta(^{1}\text{H})$	$\Delta \delta$ (¹ H)
H^1	_	_	8.184	_
H^2	7.688dd	7.569-7.602	_	-0.102^{a}
H ³	7.422td	7.558t	7.991dd	0.136 ^a
H^4	7.969d	7.978d	7.873d	0.009 ^a
H^5	7.880d	7.914d	7.889d	0.034 ^a
H^6	7.381td	7.456td	7.613td	0.075^{a}
H^7	7.484td	7.318td	7.532td	-0.166^{a}
H^8	8.222d	7.691d	7.899d	-0.531^{a}
$\mathbf{H}^{1'}$	_	8.154s	8.184s	-0.030^{b}
$H^{2'}$	7.688dd	_	_	-
$H^{3'}$	7.422td	8.190dd	7.991dd	0.199 ^b
$H^{4'}$	7.969d	7.811d	7.873d	0.062 ^b
$H^{5'}$	7.880d	7.835d	7.889d	-0.054^{b}
$H^{6'}$	7.381td	7.596–7.602m	7.613td	-0.028^{b}
$H^{7'}$	7.484td	7.449td	7.532td	-0.083^{b}
H ^{8′}	8.222d	7.759d	7.899d	-0.140^{b}
$^{a} \Delta \delta ($	20)–(16)(¹ H)			

^b $\Delta\delta(20) - (21)(^{1}\text{H})$

Table 5 ¹H-NMR chemical shifts (δ (¹H), ppm) and chemical shift differences ($\Delta\delta(^{1}H)$, ppm) of the dinaphthyl diazomethanes 17, 22, and 23

	17 , $\delta({}^{1}\text{H})$	22 , $\delta(^{1}\text{H})$	23 , $\delta({}^{1}\text{H})$	$\Delta\delta$ (¹ H)
H^1	-	-	7.497	-
H^2	7.335	7.785	_	-0.450^{a}
H ³	7.420	7.635	7.437-7.478	-0.215^{a}
H^4	7.779	7.995	7.892	-0.216^{a}
H^5	7.892	7.995	7.837	-0.103^{a}
H^6	7.497	7.576	7.437–7.478	-0.079^{a}
H^7	7.393	7.504	7.487	-0.111^{a}
H^8	7.875	7.963	7.758	-0.088^{a}
$\mathrm{H}^{1'}$	_	7.354	7.497	-0.143^{b}
$H^{2'}$	7.335	_	-	-
$H^{3'}$	7.420	7.225	7.437–7.478	-0.232^{b}
$\mathrm{H}^{4'}$	7.779	7.822	7.892	-0.070^{b}
$H^{5'}$	7.892	7.806	7.837	-0.031^{b}
$H^{6'}$	7.497	7.402	7.437-7.478	-0.055^{b}
$\mathrm{H}^{7'}$	7.393	7.438	7.487	-0.049^{b}
H ^{8′}	7.875	7.625	7.758	-0.133 ^b

^a $\Delta\delta(22) - (17)(^{1}H)$

^b $\Delta\delta(22) - (23)(^{1}\text{H})$

2,2'-dinaphthyl derivatives. Tables 6, 7, and 8 give the ¹³C-NMR chemical shifts (δ (¹³C), ppm) of the compounds 15–23 and the corresponding $\Delta\delta(^{13}C)$ values (defined analogously to the $\Delta\delta(^{1}\text{H})$ values above).

Table 6 ¹³C-NMR chemical shifts ($\delta({}^{1}C)$, ppm) and chemical shift differences ($\Delta \delta({}^{1}C)$, ppm) of the dinaphthyl ketones 15, 18, and 19

	15 , $\delta(^{13}C)$	18 , $\delta(^{13}C)$	19 , $\delta(^{13}C)$	$\Delta\delta(^{13}\text{C})$
C^1	137.14	133.77	131.82	-3.37^{a}
C^2	130.42	127.65	135.27	-2.77^{a}
C ³	124.34	124.39	125.88	0.05^{a}
C^4	132.47	131.17	128.35	-1.30^{a}
C^{4a}	133.85	136.56	135.17	2.71 ^a
C^5	128.47	128.41	127.85	-0.06^{a}
C^6	126.53	126.47	128.31	-0.06^{a}
C^7	127.83	127.24	126.83	-0.59^{a}
C^8	125.89	125.74	129.43	-0.15^{a}
C^{8a}	131.18	131.06	132.30	-0.12^{a}
$C^{1'}$	137.14	132.84	131.82	1.02 ^b
$C^{2'}$	130.42	135.70	135.27	0.43 ^b
C ^{3′}	124.34	125.36	125.88	-0.52^{b}
$C^{4'}$	132.47	128.40	128.31	0.09 ^b
$\mathrm{C}^{4\mathrm{a}'}$	133.85	135.65	135.17	0.48 ^b
C ^{5′}	128.46	127.79	127.85	-0.06^{b}
$C^{6'}$	126.53	128.63	128.31	0.32 ^b
$C^{7'}$	127.83	126.76	126.83	-0.07^{b}
$C^{8'}$	125.89	129.65	129.43	0.22 ^b
$C^{8a'}$	131.18	132.37	132.30	0.07 ^b
C=O	199.74	197.95	196.82	-1.79^{a}
				$+1.13^{b}$

Table 7 ¹³C-NMR chemical shifts (δ (¹³C), ppm) and chemical shift differences ($\Delta\delta$ (¹³C), ppm) of the dinaphthyl thioketones **16**, **20**, and 21

	16 , $\delta(^{13}C)$	20 , $\delta(^{13}C)$	21 , $\delta(^{13}C)$	$\Delta\delta(^{13}\text{C})$
C^1	148.57	147.52	129.96	-1.05^{a}
C^2	127.99	126.02	144.91	-1.97^{a}
C^3	124.79	125.04	127.15	0.25 ^a
C^4	131.68	129.60	127.83	-2.08^{a}
C^{4a}	133.98	133.50	135.05	-0.48^{a}
C^5	128.34	128.20	127.79	-0.14^{a}
C^6	126.28	126.14	128.26	-0.14^{a}
C^7	127.34	126.61	126.96	-0.73^{a}
C^8	125.77	126.14	129.77	0.37 ^a
C^{8a}	130.02	132.30	132.31	2.28 ^a
$\mathbf{C}^{1'}$	148.57	130.27	129.96	0.31 ^b
$C^{2'}$	127.99	143.45	144.91	-1.46^{b}
$C^{3'}$	124.79	125.50	127.15	-1.65 ^b
$\mathbf{C}^{4'}$	131.68	128.30	127.83	0.47 ^b
$\mathrm{C}^{4\mathrm{a}'}$	133.98	135.59	135.05	0.54 ^b
$C^{5'}$	128.34	127.77	127.79	-0.02^{b}
$C^{6'}$	126.28	128.90	128.26	0.64 ^b
$\mathbf{C}^{7'}$	127.34	126.90	126.96	-0.06^{b}
$C^{8'}$	125.77	130.37	129.77	0.60 ^b
$\mathrm{C}^{8\mathrm{a}'}$	130.02	130.05	132.31	-2.26 ^b
C=S	241.58	239.41	237.31	-2.17^{a}
				$+2.10^{b}$

^a $\Delta\delta(18) - (15)(^{13}C)$

^b $\Delta\delta(18) - (19)(^{13}C)$

Of particular interest is the effect of the functional groups (C=O, C=S, C=N₂) on the ¹³C-NMR chemical shifts $\delta(C^9)$ and the differential chemical shifts $\Delta\delta(C^9)$ between the 1,2'-dinaphthyl derivatives and the corresponding 1,1'dinaphthyl and 2,2'-dinaphthyl derivatives: for (NA)₂C=O, $\delta(C^{9})(18) - \delta(C^{9})(15) = -1.79 \text{ ppm} \text{ and } \delta(C^{9})(18) - \delta(C^{9})$ (19) = +1.13 ppm; for (NA)₂C=S, δ (C⁹)(20)– δ (C⁹)(16) = -2.17 ppm and $\delta(C^9)(20)-\delta(C^9)(21) = +2.10$ ppm; for $(NA)_2C=N_2$, $\delta(C^9)(22)-\delta(C^9)(17) = +1.57$ ppm and $\delta(C^9)$ $(22)-\delta(C^9)(23) = +1.49$ ppm. The changes in δ (C⁹) primarily reflect the changes in the partial positive charge at C^9 . In the dinaphthyl ketones and thioketones, the 1-naphthyl substituents(s) are more effective than the 2-naphthyl substituents(s) in stabilizing the dipolar structure $(NA)_2C^+-O^-$ and $(NA)_2C^+-S^-$, which leads to the decreased shielding of C^9 . The effect is reversed in the dinaphthyl diazomethane derivatives, due to the contribution of the dipolar structure $(NA)_2C^--N^+\equiv N$, in which C^9 bears a negative charge. As expected, the naphthalene carbon atoms bonded to the functional group (C^1 , C^2 , $C^{1'}$, $C^{2'}$) in the ketones and thicketones are shifted downfield due to the partial positive charge at C^9 (Tables 6, 7).

^a $\Delta\delta(20) - (16)(^{13}C)$

^b $\Delta\delta(20) - (21)(^{13}C)$

The most pronounced effect in the ¹H-NMR spectra is the downfield shifts of the protons *peri* to the carbonyl and the thiocarbonyl groups in 1,1'-dinaphthyl ketone (15) and 1,1'-dinaphthyl thioketone (16): $\delta(H^8)(15) = 8.576 \text{ ppm}$ and $\delta(H^8)(16) = 8.222$ ppm. This effect is ascribed to the diamagnetic anisotropy of the carbonyl and the thiocarbonyl groups [26]. A smaller effect is noted in 1,2'dinaphthyl ketone (18), $\delta(H^8)(18) = 8.136$ ppm, but is absent in 1,2'-dinaphthyl thioketone (20), $\delta(H^8)(20) =$ 7.691 ppm. For comparison, the respective chemical shifts in the 2-naphthyl moieties are $\delta(\text{H}^8/\text{H}^{8'}) = 7.759-7.931$. The downfield shifts of the protons peri to the carbonyl and the thiocarbonyl groups in 15, 16, and 18 together with the absence of the downfield shifts of the protons ortho to the carbonyl and the thiocarbonyl groups $(H^2/H^{2'})$ suggest the dominance of 1Z-conformation at the equilibrium in these dinaphthyl derivatives. In contrast, 20 adopts predominantly a 1E-conformation. The corresponding effects on the protons *ortho* to the carbonyl and the thiocarbonyl group in 2-naphthyl moieties are less pronounced. In 2,2dinaphthyl ketone (19) and 2,2'-dinaphthyl thioketone (21),

Table 8 ¹³C-NMR chemical shifts (δ (¹³C), ppm) and chemical shift differences ($\Delta \delta$ (¹³C), ppm) of the dinaphthyl diazomethanes 17, 22, and 23

	17 , δ(¹³ C)	22 , $\delta(^{13}C)$	23 , δ(¹³ C)	$\Delta\delta(^{13}C)$
C^1	128.67	125.46	123.37	-3.21 ^a
C^2	126.39	129.41	126.96	3.02 ^a
C ³	125.81	125.92	123.69	0.11 ^a
C^4	127.74	129.29	128.92	1.55 ^a
C^{4a}	134.50	134.37	131.73	-0.13^{a}
C^5	128.93	128.78	127.73	-0.15^{a}
C ⁶	126.12	126.36	125.61	0.24 ^a
C^7	126.33	126.75	126.64	0.42 ^a
C^8	124.78	125.28	127.31	0.50^{a}
C ^{8a}	130.53	132.07	133.91	1.54 ^a
$C^{1'}$	128.67	120.06	123.37	3.31 ^b
$C^{2'}$	126.39	129.16	126.96	2.20 ^b
$C^{3'}$	125.81	121.53	123.69	-2.16^{b}
$\mathrm{C}^{4'}$	127.74	128.74	128.92	-0.18^{b}
$C^{4a^{\prime}}$	134.50	130.84	131.73	-0.89^{b}
$C^{5'}$	128.93	127.67	127.73	-0.06^{b}
C ^{6′}	126.12	124.28	125.61	-1.33 ^b
$C^{7'}$	126.33	126.73	126.64	0.09 ^b
$C^{8'}$	124.78	126.98	127.31	-0.33^{b}
$C^{8a^{\prime}}$	130.53	133.98	133.91	0.07 ^b
C=N	58.31	59.88	58.39	$+1.57^{a}$
				$+1.49^{b}$

^a $\Delta\delta(22) - (17)(^{13}C)$

^b $\Delta\delta(22) - (23)(^{13}C)$

Table 9 The relative total andGibbs' free energies of	Х	Conform	nations			$\Delta E_{\rm Tot}$ (kJ/mol)	ΔG_{298} (kJ/mol)
dinaphthyl ketones 15, 18, and	0	1Z, 1'Z	15	C_2	М	23.37	23.95
population of their conformers	0	1Z, 1'E	15	C_1	М	29.64	27.77
Population of their contorners	0	1E, 1'E	15	C_2	М	37.71	37.92
	0	1 <i>Z</i> ,90	15	C_1	TS	33.60	34.39
	0	90,1'E	15	C_1	TS	49.59	51.13
	0	1Z, 1'Z	15	C_s	TS	60.11	61.51
	0	1Z, 2'E	18	C_1	М	10.97	9.39
	0	1Z, 2'Z	18	C_1	М	13.27	11.27
	0	1E, 2'E	18	C_1	Μ	17.39	13.99
	0	1E, 2'Z	18	C_1	Μ	18.94	16.03
	0	2E, 2'E	19	C_2	М	0.00	0.00

M minimum, TS transition state

0

0

0

0

2Z,2'E

2Z,2'Z

2E, 2'E

2Z,2'Z

19

19

19

19

 C_1

 C_2

 C_s

 C_s

Μ

Μ

TS

TS

2.22

4.13

25.61

28.32

0.04

3.65

25.68

28.75

 $\delta(H^1)(21) = 8.184$ ppm. $\delta(H^1)(19) = 8.330 \text{ ppm}$ and $\delta(\text{H}^3)(19) = 7.996 \text{ ppm}$, and $\delta(\text{H}^3)(21) = 7.991 \text{ ppm}$. It should be borne in mind that these downfield shifts of the *peri* protons $(H^8, H^{8'})$ and *ortho*-protons $H^1, H^{1'}, H^3$, and $H^{3'}$ are only effective in the Z-conformations. In solution, in each case, there is an equilibrium of the three (or four) diastereomeric conformations, which undergo fast E,Z diastereoisomerization (vide infra, "DFT study"). The relative populations of these conformations should be considered. In the dinaphthyl diazomethanes 17, 22, and 23, the analogous downfield shifts of the protons *peri* and ortho to the diazomethane group were absent, irrespective of the site of the substitution in the naphthyl group. In these derivatives, due to the contributions of the dipolar structures $(NA)_2C^--N^+\equiv N$; the effect of diamagnetic anisotropy of the diazomethane group does not come into play. The pronounced downfield shift of H^2 in 22, relative to H^2 in 17, $\Delta\delta(H^2) = -0.450$ may be due to the contribution of the 1E,2'E-conformation in **22**. For the comparison between the experimental and the DFT calculated chemical shifts, see the next section.

DFT study

DFT methods are capable of generating a variety of isolated molecular properties quite accurately, especially via the hybrid functional, and in a cost-effective way [27, 28]. The B3LYP hybrid functional was successfully employed to treat overcrowded BAEs [29, 30] and overcrowded

 $\Delta\Delta G_{298}$ (kJ/mol)

0.00

3.83

13.97

10.44 27.18

37.57 0.00

1.88

4.59

6.64 0.00

0.04

3.65

25.68

28.75

Isomer (%)

82.2

17.5

0.3

_

59.0

27.7

9.2 4.1

45.2

44.4

10.4

_

naphthologous analogues of BAEs-1, i.e., mono-bridged tetraarylenes [9]. Dinaphthyl ketones **15**, **18**, and **19**, dinaphthyl thioketones **16**, **20**, and **21**, dinaphthyl diazomethanes **17**, **22**, and **23** were subjected to a systematic computational DFT study of their conformational spaces and of their relative stabilities. The relative B3LYP/6-31G(d) energies (ΔE_{Tot}) and Gibbs free energies (ΔG_{298} and $\Delta \Delta G_{298}$) of **15–23** are presented in Tables 9, 10, and 11. Selected calculated geometrical parameters of these species are given in Tables 12, 13, and 14. The following geometrical parameters were considered: the twist angles τ_1 and τ_2 around C¹–C⁹ and C²–C⁹ naphthyl bonds; the bond angle β at a heteroatom; the dihedral angle ν between the naphthalene systems; the pyramidalization angles χ at C¹, C², and C⁹.

Conformational spaces

As noted above, the dinaphthyl derivatives **15–23** may adopt four major conformations defined by the twist angles around the C¹–C⁹ and C²–C⁹ naphthyl bonds. For each molecule, the *Z,Z-, Z,E-, E,Z-*, and *E,E*-conformations were calculated, using the symmetry constraints as indicated in Tables 9, 10, and 11. The nature of the resulting stationary points was verified by calculations of the vibrational frequencies. The *C*₂-conformations of **15–17**, **19**, **21**, and **23** were minima, whereas the *C_s*-conformations were found to be transition states for diastereomerizations, with short H¹…H^{1'} (*E,E*-conformations) or H³…H^{3'} (*Z,Z*-conformations) contact distances. The *Z,E* and *E,Z* calculated conformations of **15**, **16**, **17**, **19**, **20**, and **23** are mutually equivalent.

Table 10 The relative total and Gibbs' free energies of dinaphthyl thioketones 16, 20, and 21 and the equilibrium population of their conformers

X	Conform	natio	ns		ΔE_{Tot} (kJ/mol)	ΔG_{298} (kJ/mol)	$\Delta\Delta G_{298}$ (kJ/mol)	Isomer (%)
s	1 <i>Z</i> ,1′ <i>E</i>	16	C_1	М	39.00	37.50	0.00	65.8
S	1E, 1'E	16	C_2	Μ	39.12	40.10	2.60	23.0
S	1Z, 1'Z	16	C_2	Μ	42.58	41.88	4.38	11.2
S	1Z, 1'Z	16	C_s	TS	72.78	73.88	36.38	_
S	1E,2'E	20	C_1	Μ	16.07	13.38	0.00	52.7
S	1Z,2'E	20	C_1	Μ	18.77	15.46	2.08	22.7
S	1E,2'Z	20	C_1	Μ	18.11	16.15	2.77	17.2
S	1Z,2'Z	20	C_1	Μ	21.80	18.24	4.87	7.4
S	2E,2'E	21	C_2	Μ	0.00	0.00	0.00	50.4
S	2Z,2'E	21	C_1	Μ	2.22	0.56	0.56	40.2
S	2Z,2'Z	21	C_2	Μ	4.10	4.15	4.15	9.4
S	2E,2'E	21	C_s	TS	35.91	37.17	37.17	_
S	2Z,2'Z	21	C_s	TS	37.17	37.81	37.81	-

M minimum, TS transition state

 Table 11
 The relative total and Gibbs' free energies of dinaphthyl diazomethanes 17, 22, and 23

X	Conform	ations			ΔE_{Tot} (kJ/mol)	ΔG_{298} (kJ/mol)	$\Delta\Delta G_{298}$ (kJ/mol)
N	1Z, 1'E	17	C_1	М	24.60	25.64	0.00
Ν	1Z, 1'Z	17	C_2	Μ	26.53	28.74	3.10
Ν	1E, 1'E	17	C_2	Μ	27.78	30.63	4.99
Ν	1Z, 1'Z	17	C_s	TS	47.04	52.77	27.14
Ν	1E, 2'E	22	C_1	М	9.40	8.51	0.00
Ν	1Z, 2'E	22	C_1	М	10.06	9.65	1.14
Ν	1E,2'Z	22	C_1	М	10.35	9.82	1.31
Ν	1Z,2'Z	22	C_1	М	10.93	10.72	2.21
Ν	2Z,2'E	23	C_1	М	0.00	0.00	0.00
Ν	2Z, 2'Z	23	C_2	М	0.35	2.03	2.03
Ν	2E,2'E	23	C_2	М	0.18	2.19	2.19
Ν	2Z, 2'Z	23	C_s	TS	23.05	27.07	27.07
N	2E,2'E	23	C_s	TS	20.13	24.73	24.73

M minimum, TS transition state

Ketones 15, 18, and 19 adopt $1Z_1'Z_2$, $1Z_2'E_2$, and 2E,2'E-conformations, respectively, as their global minima (Table 9). Ketone 1Z, 1'Z-15 is the most overcrowded among these three ketones. The source of the overcrowding is the non-bonding peri-hydrogens interactions O¹⁰...H⁸ and $C^9 \cdots H^8$ and the *ortho*-hydrogen interaction $C^9 \cdots H^2$ (6-7% penetration). Ketone 1Z,1'Z-15 is also the least stable among these ketones, 24.0 kJ/mol higher in energy than 2E,2'E-19. The geometry of the 1Z,1'Z-conformation of 15 corresponds to its X-ray geometry; however, the twist angle $\tau_1(O^{10}-C^9-C^1-C^{8a}) = -34.4^\circ$ and the naphthyl dihedral angle $\theta = 67.6^{\circ}$ in 1Z.1'Z-15 are somewhat smaller than the respective angles in the X-ray geometry of 15 (Table 2). Ketone $1Z_2'E_18$ is less overcrowded than 1Z,1'Z-15 and is only 9.4 kJ/mol less stable than 2E,2'E-19. The 1E,2'E-conformation of 18, which is 4.6 kJ/mol higher in energy than the global minimum 1Z,2'E-18, corresponds well with its X-ray geometry. The twist angles $\tau_2(O^{10}-C^9-C^1-C^{8a}) = 52.2^\circ, \ \tau_2(O^{10}-C^9-C^{2'}-C^{1'}) = 14.5^\circ$ and the naphthyl dihedral angle $\theta = 68.1^{\circ}$ in 1E, 2'E-18 are close to the geometry of its X-ray structure (Table 2). Ketone 2E,2'E-19 lacks peri-hydrogen interactions and is devoid of overcrowding. The X-ray geometry of 19 is described by the 2Z,2'Z-19 conformations. It is 3.7 kJ/mol higher in energy than the global minimum $2E_{,2}^{\prime}E_{-19}$. The twist angle $\tau_1(O^{10}-C^9-C^2-C^1) = -26.8^\circ$ and the naphthyl dihedral angle $\theta = 51.1^{\circ}$ in 2Z,2'Z-19 are very close to the respective angles in the X-ray structure of 19 (Table 2).

Thioketones 16, 20, and 21 adopt 1Z,1'E-, 1E,2'E-, and 2E,2'E-conformations, respectively, as their global minima (Table 10). Like 1Z,1'Z-15, thioketone 1Z,1'E-16 is the most overcrowded among these thioketones due to the

 Table 12 Selected geometrical parameters of 1,1'-dinaphthyl derivatives 15, 16, and 17

X	Conform	ation			ΔG_{298} (kJ/mol)	$\Delta\Delta G_{298}$ (kJ/mol)	τ_1^a (°)	$\tau_2^{\ b}$ (°)	β^{c} (°)	$\chi(C^9)^d$ (°)	$\begin{array}{c} \chi(C^1)^d \\ \chi(C^{1'})^d \ (^\circ) \end{array}$	θ ^e (°)
0	1 <i>Z</i> ,1′Z	15	C_2	М	23.95	0.00	-34.4	141.1	118.5	0.0	4.5	67.6
0	1Z, 1'E	15	C_1	Μ	27.77	3.83	-29.4	146.9	119.6	-4.4	3.7	72.4
							130.7	-46.3			-3.0	
0	1E, 1'E	15	C_2	Μ	37.92	13.97	138.2	-39.4	122.6	0.0	-2.4	71.5
0	1 <i>Z</i> ,90	15	C_1	TS	34.39	10.44	1.6	-178.6	118.7	-0.4	0.2	88.7
							-89.7	85.7			4.6	
0	90,1'E	15	C_1	TS	51.13	27.18	88.4	-85.7	123.9	-0.8	-6.0	88.5
							-179.4	0.6			0.1	
0	1Z, 1'Z	15	C_s	TS	61.51	37.57	-49.5	127.9	121.0	5.0	2.6	47.0
S 12	1Z, 1'E	16	C_1	Μ	37.50	0.00	-45.4	131.3	117.2	6.1	3.3	83.6
							132.5	-47.3			-0.1	
S	1E, 1'E	16	C_2	Μ	40.10	2.60	135.2	-44.0	120.6	0.0	-0.9	75.4
S	1Z, 1'Z	16	C_2	Μ	41.88	4.38	-45.7	131.5	115.6	0.0	2.8	87.1
S	1Z, 1'Z	16	C_s	TS	73.88	36.38	70.2	-108.9	117.7	2.1	1.0	58.5
Ν	1Z, 1'E	17	C_1	Μ	25.64	0.00	-47.1	132.9	124.9	11.8	0.0	81.8
							135.8	-43.2			-1.0	
Ν	1Z, 1'Z	17	C_2	Μ	28.74	3.10	-45.3	134.6	123.7	0.0	0.1	82.5
Ν	1E, 1'E	17	C_2	М	30.63	4.99	135.1	-43.3	129.0	0.0	-1.5	77.2
Ν	1Z, 1'Z	17	C_s	TS	52.77	27.14	-58.7	121.5	126.7	-0.1	-0.2	44.8

M minimum, TS transition state

^a X^{10} - C^9 - C^1 - C^{8a}/X^{10} - C^9 - $C^{1'}$ - $C^{8a'}$ torsion angles

^b $X^{10}-C^9-C^1-C^2/X^{10}-C^9-C^{1'}-C^{2'}$ torsion angles

^c $C^1-C^9-C^{1'}$ bond angle

^d $\chi(C^9)$ —the improper torsion angle $C^1 - C^9 - X^{10} - C^{1'} - 180^\circ \pmod{360^\circ}$; $\chi(C^1)/\chi(C^{1'})$ —the improper torsion angles $C^{8a} - C^1 - C^9 - C^2/C^{8a'} - C^{1'} - C^9 - C^{2'}$, respectively, $-180^\circ \pmod{360^\circ}$

^e The dihedral angle between the least-square planes of the carbon atoms of the naphthyl moieties

short non-bonding distances (9–11% penetration) to *peri*hydrogens S¹⁰...H⁸, C⁹...H⁸, and C⁹...H². Its twist angles $\tau_1(S^{10}-C^9-C^1-C^{8a}) = -45.4^{\circ}$ and $\tau_1(S^{10}-C^9-C^{1'}-C^{8a'}) =$ 132.5° and the naphthyl folding angle $\theta = 83.6^{\circ}$ correspond well with the X-ray structure of **16** (Table 2). The local minimum 1*Z*,1′*Z*-**16** conformation is 4.4 kJ/mol less stable than 1*Z*,1′*E*-**16**, and it features the small bond angle $\beta(C^1-C^9-C^{1'}) = 115.6^{\circ}$ due to the need to accommodate a larger sulfur atom, as compared to oxygen. Thioketone 1*Z*,1′*E*-**16** is the least stable among **16**, **20**, and **21**, 37.5 kJ/ mol higher in energy than 2*E*,2′*E*-**21**. Thioketones 1*E*,2′*E*-**20** and 2*E*,2′*E*-**21** are less overcrowded than 1*Z*,1′*E*-**16**; 1*E*,2′*E*-**20** is 13.4 kJ/mol higher in energy than 2*E*,2′*E*-**21**.

Dinaphthyl diazomethanes **17**, **22**, and **23** adopt 1Z, 1'E-, 1E, 2'E-, and 2Z, 2'E-conformations, respectively, as their global minima (Table 11). The least stable 1Z, 1'E-**17** is 25.6 kJ/mol higher in energy than 2E, 2'E-**23** and the most overcrowded of the three constitutional isomers (6–8% penetration due to the short non-bonding distances N¹⁰…H⁸ and C⁹…H²/C⁹…H²/). Dinaphthyl diazomethane 1E, 2'E-**22**

is 8.5 kJ/mol higher in energy than $2E_{,2}'E_{-23}$, both are not overcrowded.

The interconversion of the conformations in the dinaphthyl derivatives 15-23 may be illustrated by ketone 15. The global minimum C_2 -1Z,1'Z-conformation undergoes diastereomerization to the C_1 -1Z,1'E conformation by rotating the 1'-naphthyl moiety around $C^{1'}-C^9$ bond via the 1Z,90 transition state, with energy barrier of 10.4 kJ/mol. The naphthyl moieties in this transition state are nearly orthogonal ($\theta = 88.7^{\circ}$), and the carbonyl group is aligned with one 1-naphthyl moiety ($\tau_1 = 1.6^\circ$) and is perpendicular to the other ($\tau_1 = 89.7^\circ$). The local minimum C_1 -1Z,1'E conformation, which is 3.8 kJ/mol higher in energy than the global minimum, undergoes diastereomerization into the second local minimum C_2 -1E,1'E conformation (14.0 kJ/mol higher in energy than the global minimum) by rotating the 1-naphthyl moiety around $C^{1}-C^{9}$ bond via the 90,1'E transition state, with a higher energy barrier of 23.4 kJ/mol. The naphthyl moieties in this transition state are also nearly orthogonal ($\theta = 88.5^{\circ}$). The

 $\begin{array}{l} \chi(C^1)^d \\ \chi(C^{2'})^d \; (^\circ) \end{array}$ $\chi(C^9)^d$ (°) X τ_2^{b} (°) β^{c} (°) θ^{e} (°) Conformations ΔG_{298} (kJ/mol) $\Delta\Delta G_{298}$ (kJ/mol) τ_1^a (°) 0 1Z, 2'E18 C_1 М 9.39 0.00 -39.7 135.9 119.8 0.7 4.4 59.4 156.2 -19.4-4.40 1Z, 2'Z18 C_1 Μ 11.27 1.88 -38.3137.4 119.5 1.2 4.4 58.4 -21.7155.1 3.2 0 1E, 2'E18 C_1 Μ 13.99 4.59 -125.052.2 120.5 4.0 2.8 68.1 -161.714.5 3.8 1E, 2'Z-127.00 18 C_1 Μ 16.03 6.64 50.4 120.4 3.7 2.6 66.2 16.0 -160.9-3.0S 1E, 2'E20 C_1 Μ 13.38 0.00 -119.859.2 118.2 2.3 0.9 74.5 -157.719.9 2.4 S 1Z, 2'E2.08 2.8 20 C_1 Μ 15.46 -58.3119.0 117.3 2.6 74.6 158.7 -18.9-2.6S 1E, 2'Z20 C_1 М 16.15 2.77 -123.855.7 118.1 0.5 72.5 2.6 23.6 -154.8-1.6S 1Z, 2'Z20 C_1 Μ 18.24 4.87 -56.0121.3 116.9 3.0 2.7 74.1 -23.4155.4 1.2 1E, 2'E1.0 Ν 22 C_1 Μ 8.51 0.00 -114.864.2 125.7 3.9 72.8 -169.610.1 0.3 120.2 0.6 1Z, 2'E22 1.14 -59.2125.5 66.1 Ν C_1 Μ 9.65 2.9 169.1 -10.2-0.7Ν 1E, 2'Z22 C_1 Μ 9.82 1.31 -119.1 59.6 126.1 2.8 1.2 71.8 15.1 -164.0-0.9 2.21 0.5 Ν 1Z,2'Z22 C_1 Μ 10.72 -55.5124.0 125.6 4.7 66.0 -14.5164.0 1.4

Table 13 Selected geometrical parameters of 1,2'-dinaphthyl derivatives 18, 20, and 22

M minimum, TS transition state

^a X^{10} - C^9 - C^1 - C^{8a}/X^{10} - C^9 - $C^{2'}$ - $C^{1'}$ torsion angles

^b $X^{10}-C^9-C^1-C^2/X^{10}-C^9-C^{2'}-C^{3'}$ torsion angles

^c $C^1 - C^9 - C^{2'}$ bond angle

^d $\chi(C^9)$ —the improper torsion angle $C^1 - C^9 - X^{10} - C^{2'} - 180^\circ \pmod{360^\circ}$; $\chi(C^1)/\chi(C^{2'})$ —the improper torsion angles $C^{8a} - C^1 - C^9 - C^2/C^{1'} - C^{2'} - C^9 - C^{3'}$, respectively, $-180^\circ \pmod{360^\circ}$

^e Dihedral angle between the least-square planes of the carbon atoms of the naphthyl moieties

diastereomerization in the reverse direction leads from C_2 -1E,1'E-15 to C_1 -1E,1'Z-15 with the energy barrier of 13.2 kJ/mol, and from C_1 -1E,1'Z-15 to C_2 -1Z,1'Z-15 with the energy barrier of 6.6 kJ/mol. The achiral C_s -1Z,1'Z-15 conformation serves as a transition state for enantiomerization of chiral C_2 -1Z,1'Z-15. The simultaneous rotation of two naphthyl moieties toward each other requires a short contact H^2 ··· $H^{2'}$ distance, which leads to a high energy barrier, 37.6 kJ/mol.

Relative stabilities

The relative thermodynamic stabilities of 1- and 2-substituted naphthalenes are governed by both steric and electronic effects. Based on elementary resonance considerations, there are seven dipolar resonance structures for

1-substituted naphthalene derivatives $1-(NA)_2C=X$ (X = O, N, S), of which four preserve the aromatic sextet, while there are only six dipolar resonance structures for 2-substituted naphthalene derivatives 2-(NA)₂C=X, of which only two preserve the aromatic sextet. The positive charge in the dipolar resonance structures is more efficiently delocalized in 1-(NA)₂C=X than in 2-(NA)₂C=X. On the other hand, the 1-substituted naphthalenes are destabilized by the repulsive interactions between the substituent and the hydrogen at the peri position. In each series of constitutional isomers of dinaphthyl derivatives 15–23, the order of stabilities is 2,2'-(NA)₂C=X > 1,2'- $(NA)_2C=X > 1,1'-(NA)_2C=X$. Moreover, in each series the energy difference $\Delta\Delta G_{298}$ between 1,1'-(NA)₂C=X and 1,2'-(NA)₂C=X is two-three times larger than $\Delta\Delta G_{298}$ between 1,2'-(NA)₂C=X and 2,2'-(NA)₂C=X (Tables 9, 10,

 Table 14
 Selected geometrical parameters of 2,2'-dinaphthyl derivatives 19, 21, and 23

X	Conform	ations			ΔG_{298} (kJ/mol)	$\Delta\Delta G_{298}$ (kJ/mol)	$\tau_1{}^a$ (°)	$\tau_2^{\ b} (^{\circ})$	β^{c} (°)	$\chi(C^9)^d$ (°)	$\begin{array}{c} \chi(C^2)^d \\ \chi(C^{2'})^d \ (^\circ) \end{array}$	θ ^e (°)
0	2E,2'E	19	C_2	М	0.00	0.00	149.8	-25.4	121.0	0.0	-4.8	51.7
0	2Z,2'E	19	C_1	Μ	0.04	0.04	-27.4	149.2	120.7	0.6	3.4	51.3
							150.7	-24.4			-4.9	
0	2Z,2'Z	19	C_2	М	3.65	3.65	-26.8	149.9	120.3	0.0	3.4	51.1
0	2E,2'E	19	C_s	TS	25.68	25.68	-159.6	18.7	125.9	4.5	1.7	20.3
0	2Z,2'Z	19	C_s	TS	28.75	28.75	22.5	-157.0	124.7	5.9	0.5	27.1
S	2E,2'E	21	C_2	М	0.00	0.00	144.6	-31.5	118.4	0.0	-3.9	61.4
S	2Z,2'E	21	C_1	Μ	0.56	0.56	-35.6	142.3	118.1	-0.3	2.1	61.4
							146.5	-30.0			-3.5	
S	2Z,2'Z	21	C_2	М	4.15	4.15	-33.8	144.4	117.8	0.0	1.9	60.9
S	2E,2'E	21	C_s	TS	37.17	37.17	136.1	-42.4	121.7	5.0	1.5	41.0
S	2Z,2'Z	21	C_s	TS	37.81	37.81	46.0	-134.4	120.3	5.6	0.4	48.1
Ν	2Z,2'E	23	C_1	Μ	0.00	0.00	-33.0	144.8	126.5	-1.0	2.3	53.6
							154.1	-25.0			-0.9	
Ν	2Z,2'Z	23	C_2	Μ	2.03	2.03	-30.0	148.1	126.2	0.0	1.9	55.6
Ν	2E,2'E	23	C_2	Μ	2.19	2.19	151.4	-27.4	127.0	0.0	1.2	50.1
Ν	2Z,2'Z	23	C_s	TS	27.07	27.07	-32.0	-146.8	129.6	-10.3	1.2	33.4
Ν	2E,2'E	23	C_s	TS	24.73	24.73	153.0	-27.2	130.6	6.9	0.2	29.0

M minimum, TS transition state

^a $X^{10}-C^9-C^2-C^1/X^{10}-C^9-C^{2'}-C^{1'}$ torsion angles

^b X^{10} - C^9 - C^2 - C^3/X^{10} - C^9 - $C^{2'}$ - $C^{3'}$ torsion angles

^c C²–C⁹–C^{2'} bond angle

^d χ (C⁹)—the improper torsion angle C²–C⁹–X¹⁰–C^{2'} – 180° (mod 360°); χ (C²)/ χ (C^{2'})—the improper torsion angles C¹–C²–C⁹–C³/C^{1'}–C^{2'}–C⁹–C^{3'}, respectively, –180° (mod 360°)

^e The dihedral angle between the least-square planes of the carbon atoms of the naphthyl moieties

11). The destabilization of the 1,1'-dinaphthyl derivatives relative to their 1,2'- and 2,2'-constitutional isomers stems probably from the overcrowding due to repulsive nonbonding interactions $X^{10} \cdots H^8/X^{10} \cdots H^{8'}$, $C^9 \cdots H^2/C^9 \cdots H^{2'}$, and $C^9 \cdots H^8/C^9 \cdots H^{8'}$. These repulsive interactions cause the carbonyl group to tilt out of the aromatic plane, thus decreasing its conjugation with the naphthyl moiety. Indeed, the mean values of the τ_1 twist angles in all the conformations of dinaphthyl ketones decrease in the 1,1 > 1,2 > 2,2 series: 39° (15), 33° (18), and 28° (19). The same order of the decrease of the twist angles is observed in dinaphthyl thioketones, 46° (16), 40° (20), 35° (21), and in dinaphthyl diazomethanes, 45° (17), 37° (22), 29° (23).

In considering the global minimum for each constitutional isomer, the emerging picture is not uniform. In the dinaphthyl ketone series, the most stable conformations are 1Z,1'Z, 1Z,2'E, and $2E,2'E \approx 2Z,2'E$. In the dinaphthyl thioketone series, the most stable conformations are 1Z,1'E, 1E,2'E, and 2E,2'E. In the dinaphthyl diazomethane series, the most stable conformations are 1Z,1'E, 1E,2'E, and 2Z,2'E. Thus, with the increase of the radius of a

 Table 15 Experimental and calculated ¹H-NMR chemical shifts of the conformations of dinaphthyl ketone 15 and their equilibrium percentages

	Exp.	Calculated					
		1 <i>Z</i> ,1′ <i>Z</i> 82.2%	1 <i>Z</i> ,1′ <i>E</i> 17.5%	1 <i>E</i> ,1′ <i>E</i> 0.3%	At equilibrium		
H^2	7.616	7.44	7.22	8.14	7.47		
H ³	7.440	7.30	7.13	7.60	7.31		
H^4	8.033	7.77	7.73	7.81	7.77		
H^5	7.954	7.70	7.68	7.61	7.69		
H^6	7.588	7.51	7.52	7.19	7.49		
H^7	7.588	7.60	7.67	6.86	7.56		
H^8	8.576	8.92	9.27	7.22	8.81		
$H^{2'}$			7.92				
$H^{3'}$			7.54				
$H^{4'}$			7.79				
$H^{5'}$			7.68				
$H^{6'}$			7.31				
$H^{7'}$			7.07				
H ^{8′}			7.39				

Table 16 Experimental and calculated ¹H-NMR chemical shifts ofthe conformations of dinaphthyl ketone**18** and their equilibriumpercentages

	Exp.	Calculated						
		1 <i>Z</i> ,2' <i>E</i> 59.0%	1 <i>Z</i> ,2' <i>Z</i> 27.7%	1 <i>E</i> ,2' <i>E</i> 9.2%	1 <i>E</i> ,2′ <i>Z</i> 4.1%	At equilibrium		
H^2	7.657	7.63	7.57	7.75	7.78	7.63		
H^3	7.558	7.38	7.36	7.53	7.54	7.40		
H^4	8.052	7.80	7.78	7.82	7.80	7.79		
H^{5}	7.963	7.71	7.69	7.72	7.71	7.70		
H^{6}	7.558	7.49	7.50	7.37	7.37	7.48		
H^{7}	7.514	7.55	7.57	7.18	7.19	7.51		
H^{8}	8.136	8.69	8.73	7.62	7.55	8.56		
H^{1^\prime}	8.264	7.89	8.76	7.51	8.80	8.13		
H^{3^\prime}	8.095	8.40	7.59	8.45	7.18	8.13		
$\mathrm{H}^{4'}$	7.948	7.79	7.58	7.77	7.38	7.71		
$\mathrm{H}^{5'}$	7.911	7.69	7.68	7.66	7.59	7.68		
$\mathrm{H}^{6'}$	7.615	7.50	7.52	7.47	7.52	7.50		
$\mathrm{H}^{7'}$	7.514	7.41	7.50	7.29	7.49	7.43		
$\mathrm{H}^{8'}$	7.833	7.63	7.96	7.33	7.96	7.71		

Table 17Experimental and calculated ¹H-NMR chemical shifts ofthe conformations of dinaphthyl ketone19 and their equilibriumpercentages

Exp.	Calculate	Calculated					
	2 <i>E</i> ,2' <i>E</i> 45.2%	2Z,2'E 44.4%	2Z,2'Z 10.4%	At equilibrium			
8.330	8.05	8.59	8.59	8.21			
7.997	8.24	7.79	7.71	8.09			
7.997	7.78	7.63	7.63	7.73			
7.945	7.71	7.69	7.69	7.70			
7.635	7.54	7.53	7.54	7.53			
7.571	7.45	7.51	7.48	7.46			
7.931	7.69	7.92	7.91	7.76			
		7.99					
		8.26					
		7.77					
		7.70					
		7.51					
		7.43					
		7.69					
	Exp. 8.330 7.997 7.997 7.945 7.635 7.571 7.931	Exp. Calculate 2E,2'E 45.2% 8.330 8.05 7.997 8.24 7.997 7.78 7.945 7.71 7.635 7.54 7.931 7.69	Exp.Calculated $2E,2'E$ 45.2% $2Z,2'E$ 44.4% 8.3308.058.597.9978.247.797.9977.787.637.9457.717.697.6357.547.537.5717.457.517.9317.697.927.998.267.777.707.517.437.697.69	Exp.Calculated $2E,2'E$ 45.2% $2Z,2'E$ 44.4% $2Z,2'Z$ 10.4% 8.3308.058.598.597.9978.247.797.717.9977.787.637.637.9457.717.697.697.6357.547.537.547.5717.457.517.487.9317.697.927.917.998.267.777.707.517.437.697.69			

heteroatom at C⁹, $r_{\rm O} < r_{\rm N} < r_{\rm S}$, the *E*-conformations become more favorable. The reason for this trend is the increase in overcrowding of the *Z*-conformations due to the short non-bonding X¹⁰...H⁸ distances, e.g., 225.7 pm (7.5% penetration) for 1*Z*,1'*Z*-**15**, 242.6 pm (8.5% penetration) for 1*Z*,1'*Z*-**17**, and 266.9 pm (10.7% penetration) for 1*Z*,1'*Z*-**16**. In addition, the absolute values of the twist angles of the *Z*-conformations increase more than those of the *E*-conformations, e.g., $|\tau_1| = 34.4^{\circ}$ (1*Z*,1′*Z*-15) versus $|\tau_2| = 39.4^{\circ}$ (1*E*,1′*E*-15) for a ketone, and $|\tau_1| = 45.7^{\circ}$ (1*Z*,1′*Z*-16) versus $|\tau_2| = 44.0^{\circ}$ (1*E*,1′*E*-16) for a thioketone. For 2,2′-substituted naphthalenes the effect is less pronounced: $|\tau_1| = 26.8^{\circ}$ (2*Z*,2′*Z*-19) versus $|\tau_2| = 25.4^{\circ}$ (2*E*,2′*E*-19) for a ketone, and $|\tau_1| = 33.8^{\circ}$ (2*Z*,2′*Z*-21) versus $|\tau_2| = 31.5^{\circ}$ (2*E*,2′*E*-21) for a thioketone. However, the energy differences ($\Delta\Delta G_{298}$) within the three/four conformations of each constitutional isomer are relatively small, 0.04–6.6 kJ/mol.

The comparison between the X-ray structures of dinaphthyl ketones and thioketones and their respective calculated geometries deserves attention. B3LYP/6-31(d) calculations satisfactorily describe the X-ray geometries of **15** and **19** (1Z,1'Z-conformation), **16** (1Z,1'*E*-conformation), and **18** (1E,1'E-conformation). 1Z,1'Z-**15** and 1Z,1'E-**16** are indeed the global minima. 1E,2'E-**18** and 2Z,2'Z-**19** are, however, local minima, being less stable than the respective global minima (1Z,2'E-**18** and 2E,2'E-**19**) by 4.6 and 3.7 kJ/mol, respectively. The stabilization of 1E,2'E-**18** and 2Z,2'Z-**19** in their respective crystal structures stems from the intermolecular interactions in crystals, which can readily dominate and suppress any preference any other conformation, especially in the cases of low energy differences between them.

Calculated NMR chemical shifts

The dinaphthyl derivatives 15-23 may adopt various conformations with relatively low energy differences (0.04-6.6 kJ/mol, excluding 1E, 1'E-15). The calculated energy barriers (Tables 9, 10, 11) do not exceed 38 kJ/mol, suggesting swift diastereomerizations on the NMR time scale (at room temperature). In order to predict correctly the experimental chemical shifts of 15–23, the equilibrium population of each of the conformers should be taken into account. Tables 9 and 10 show the equilibrium population of the conformers of dinaphthyl ketones and thioketones, respectively, calculated from their relative energies using the Boltzmann distribution values. The nuclear magnetic shielding tensors for ¹H and ¹³C of each of the conformers of the dinaphthyl ketones and thioketones under study were calculated at the B3LYP/6-31G(d)//GIAO level. The calculated chemical shifts were then multiplied by the percentages of the respective conformers at equilibrium (at room temperature) and summed.

In 15, 16, and 18, 1*Z*-conformations dominate in the equilibrium in a good agreement with the downfield shifts of H^8 protons *peri* to the carbonyl and the thiocarbonyl groups. In 20, the 1E,2'E-conformation is the global minimum, which is supported by the absence of the downfield shifts of H^8 in 20. Tables 15, 16, and 17 show the comparison between the experimental and the calculated

¹H-NMR chemical shifts of dinaphthyl ketones 15, 18, and **19**, respectively. The calculated ¹H- and ¹³C-NMR chemical shifts are in a satisfactory agreement with the respective experimental chemical shifts. The calculations correctly predict the downfield shift of the H⁸ protons *peri*- to the carbonyl and the thiocarbonyl groups in 15, 16, and 18. As expected, in 1,2-dinaphthyl ketone (18) and 1,2-dinaphthyl thicketone (20) only 1Z.2'Z- and 1Z.2'E-conformations exhibit the downfield shift of H⁸ protons. The combined equilibrium populations of these conformers are 86.7% in 18, but only 30.1% in 20, which explains the absence of the experimentally observed downfield shift of H⁸ in the latter. The calculations give the following differential chemical shifts $\Delta\delta(C^9)$ between the 1,2'-dinaphthyl derivatives and the corresponding 1,1'-dinaphthyl and 2,2'-dinaphthyl derivatives: for (NA)₂C=O, $\delta(C^9)(18) - \delta(C^9)(15) =$ -2.75 ppm and $\delta(C^9)(18)-\delta(C^9)(19) = +1.95$ ppm; for $(NA)_2C=S, \ \delta C^9)(20)-\delta(C^9)(16) = -2.74 \text{ ppm} \text{ and } \delta(C^9)$ $(20)-\delta(C^9)(21) = +4.37$ ppm. These values are in line with the measured differential chemical shifts (vide supra). The B3LYP/6-31G(d) calculations do not, however, correctly reflect the expected change in the partial positive charge at C⁹ of 1,1'-dinaphthyl, 1,2'-dinaphthyl and 2,2'dinaphthyl derivatives. The NBO natural charges at C⁹ of 15, 18, and 19 are 0.55, 0.56, and 0.55, respectively. The NBO natural charges at C^9 of 16, 20, and 22 are -0.11, -0.09, and -0.11, respectively (the Mulliken charges are identical, 0.32).

Conclusions

The crystal structures of 1,1'-dinaphthyl ketone (15), 1,2'dinaphthyl ketone (18), 2,2'-dinaphthyl ketone (19), and 1,1'-dinaphthyl thicketone (16) feature conformations with naphthyl moieties twisted around C^1-C^9/C^2-C^9 bonds. The twist angles τ_1/τ_2 are notably larger for 1Z/1E-conformations $(34^\circ-52^\circ)$ than for 2*E*/2*Z*-conformation $(15^\circ-27^\circ)$. The B3LYP/6-31G* calculated structures of 15, 16, 18, and **19** are in a good agreement with the crystal structures. The NMR experiments demonstrate the downfield shifts of the protons *peri* to the carbonyl and the thiocarbonyl groups in 15, 16, and 18, but not in 20, suggesting the predominance of 1Z-conformations in the former and of 1E-conformations in the latter. The B3LYP/6-31G* relative stabilities of dinaphthyl ketones and thioketones and calculated chemical shifts are in agreement with the NMR experimental results. In each series of constitutional isomers of dinaphthyl ketones, thioketones and diazomethanes, the order of stabilities is $2,2'-(NA)_2C=X > 1,2'-(NA)_2C=X > 1,1'-$ (NA)₂C=X. The presence of a 2-naphthyl moiety confers an E-conformation, while two 1-naphthyl moieties are needed for a Z,Z-conformation. The preference of *E*-conformations is also dependant on the heteroatom X in each $(NA)_2C=X$ series, raising with the increase of the radius of an heteroatom: O < N < S.

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