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A DIPOLE MOMENT STUDY OF 2-BENZOYLPYRROLES, DI-(2-PYRRYL)KETONES AND THEIR SULPHUR ANALOGUES

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ABSTRACT

Examination of the electric dipole moments of 2-benzoylpyrrole and di-(2-pyrryl)-ketone, and of their sulphur analogues, measured in cyclohexane and/or carbon tetrachloride, benzene and dioxane, allows their preferred conformations in these media to be determined. 2-Benzoyl-*N*-methylpyrrole and di-(2-*N*-methylpyrryl)ketone, and the corresponding thioketones, were examined in benzene and their conformations elucidated. The dipole moments of the retained conformers were all deduced from that of the closed-ring 1,1′-methylene-2,2′-dipyrrylketone. Di-(2-pyrryl)ketone and di-(2-pyrryl)thioketone uniplanar conformers were examined by the CNDO/2 technique. Further, the factors that determine the preferred conformations of these compounds were discussed briefly.

INTRODUCTION

Contrary to formyl- and acetylpyrroles, which have been extensively studied [1—4], there has been little study on 2-benzoylpyrrole [5, 6] and no structural work has been published dealing with 2-benzoyl-*N*-methylpyrrole, di(2-pyrryl)ketone and di(2-*N*-methylpyrryl)ketone, and their sulphur analogues.

In the present study, with the aim of elucidating their solution-state conformations, the electric dipole moments of 2-benzoylpyrrole and 2-thiobenzoylpyrrole, 2-benzoyl-*N*-methylpyrrole and 2-thiobenzoyl-*N*-methylpyrrole, di-(2-pyrryl)ketone and di-(2-pyrryl)thioketone, di-(2-*N*-methylpyrryl)ketone and di-(2-*N*-methylpyrryl)thioketone were measured at 30.0°C with a specified nonpolar medium as solvent. The dipole moment of 1,1′-methylene-2,2′-dipyrrylketone was determined in benzene solution.

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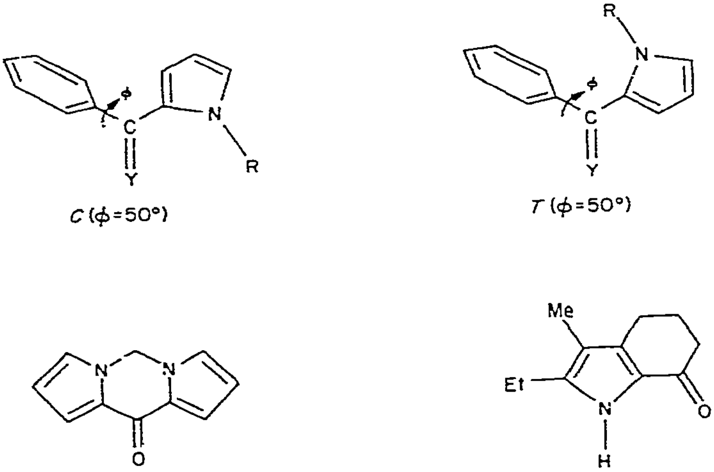
RESULTS AND DISCUSSION

Table 1 lists the electric dipole moments* of the compounds examined here and those of pyrroles and benzophenones taken from literature.

2-Benzoylpyrroles, 2-thiobenzoylpyrroles, di-(2-pyrryl)ketones and di-(2-pyrryl)thioketones will be successively examined.

The solution-state conformations of 2-benzoylpyrrole and 2-benzoyl-N-methylpyrrole

2-Benzoylpyrrole and 2-benzoyl-*N*-methylpyrrole can exist in a number of conformations, among which the more stable are those (*C* and *T*) having their (2-pyrryl-carbonyl) residue uniplanar ($\phi' = 0°$) and their phenyl group rotated by a finite ϕ angle (Fig. 1). This is because 2-benzoylpyrrole, as a solute in cyclohexane [5] and in the crystalline state [6], exhibits asymmetric *C* models in which the (2-pyrryl-carbonyl) residue is uniplanar and the phenyl group is rotated by 55 ± 10° and 50.1°, respectively. The conjugation energy of 2-formyl-*N*-methylpyrrole is much higher than that of benzaldehyde, being 52.2 [12] or 53 [13] as against 27 kJ mol^{-1} [14]. A greater decrease in the carbonyl stretching frequency is observed on passing from acetone (1719 cm^{-1}, CCl_4) to 2-benzoylpyrrole (1630, benzene)



C (φ=50°)

T (φ=50°)

Fig. 1. Retained conformers for 2-benzoylpyrrole and 2-benzoyl-*N*-methylpyrrole and their sulphur analogues; 1,1'-methylene-2,2'-dipyrrylketone and 2-ethyl-4,5-dihydro-3-methylindol-7(6H)-one.

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*Throughout this paper the electric dipole moments are expressed in Debye units, which are still widely used and which fit the molecular structure better (1 Debye (D) = 3.3356 × 10^{-30} C m). μ_s designates an experimental dipole moment in the specified solvent s (c, t, b and d stand for cyclohexane, carbon tetrachloride, benzene and dioxane, respectively), M_s a moment calculated by additivity as indicated in the text.

TABLE 1

Experimental dipole moments of pyrrole and various aromatic ketones and thioketones (Debye units)

Compound	μ_c	μ_t	μ_b	μ_d
Pyrrole	1.74[3]	1.77[3]	1.84[2]	2.09[2]
N-Methylpyrrole	1.96[3]	1.92[3]	1.95[3]	2.03[7]
Benzophenone	3.00[8]	3.03[9]	3.00[9]	3.05[10]
Thiobenzophenone	—	—	2.86[11]	—
2-Benzoylpyrrole	1.76[a]	1.91	1.88	1.95
2-Thiobenzoylpyrrole	—	2.37	2.63	2.57
2-Benzoyl-*N*-methylpyrrole	—	—	2.08	—
2-Thiobenzoyl-*N*-methylpyrrole	—	—	2.70	—
Di-(2-pyrryl)ketone	—	0.87	1.06	1.16
Di-(2-pyrryl)thioketone	1.46	1.62	1.63	1.73
Di-(2-*N*-methylpyrryl)ketone	—	—	1.05	—
Di-(2-*N*-methylpyrryl)thioketone	—	—	2.00	—
1,1'-Methylene-2,2'-dipyrrylketone	—	—	5.11	—

[a] Lit. μ = 1.27 D (for ${}_EP + {}_AP = R_D$) [5]; see Experimental for possible origin of the discrepancy with our figure.

or 2-benzoyl-*N*-methylpyrrole (1636, CCl_4) than going from acetone to benzophenone (1660, CCl_4)*. The accurate experimental refraction (R_D) of 2-benzoyl-*N*-methylpyrrole (57.7 [15]) is 1.5 cm^3 higher than the value calculated from those of benzophenone (56.7 [16], indicating an optical exaltation of 1.1 cm^3 [17]), *N*-methylpyrrole (25.7 [18]) and benzene (26.2). Ab initio calculated π charges at the oxygen atom in benzaldehyde and 2-formylpyrrole also indicate a greater (residue-carbonyl) conjugation in the latter [19, 20].

With the assumption that in both *C* and *T* conformers the phenyl-group rotational angles (φ) are similar to the value (+ and —30°) in conrotatory benzophenone [21], which is only approximately true, the dipole moments of 2-benzoylpyrrole and 2-benzoyl-*N*-methylpyrrole conformers can be calculated by using the vectorial equations

$$\mathbf{M}_s = \mu_s(Ph_2C{=}O) + \mu_s(\text{pyrrole or } N\text{-methylpyrrole}) + \Delta\mathbf{m}_s \qquad (1)$$

where $\Delta\mathbf{m}_s$ vector [directed along the (2-pyrryl-carbonyl) mesomeric moment $\mathbf{m}^*$], if any, originates from the fact that the m^* value can differ from that of $m(PhC{=}O)$ in $Ph_2C{=}O$. For weakly acidic 2-benzoylpyrrole as a solute in dioxane, and in benzene to a lesser extent, the Δm_s term should be somewhat increased relative to that in nonbasic solvents (cyclohexane and carbon

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*The decrements observed (89 and 83, and 59 cm^{-1}) are too large to be ascribed only to the nitrogen σ-inductive effect existing in 2-benzoylpyrrole and 2-benzoyl-*N*-methylpyrrole and, for 2-benzoylpyrrole, to the intramolecular N—H···O=C hydrogen bond to be present.

tetrachloride) by a specific solvent effect which will be explained later.

Examination of the benzene dipole moment of 1,1′-methylene-2,2′-dipyrrylketone shown in Fig. 1 (μ = 5.11 D), which can be regarded as uniplanar and practically rigid [22], can provide a significant value for the $\Delta \mathbf{m}_s$ term (s = c or t). Taking CNC = 109.2°, NCC(O) = 120.6° and CCO = 121.6° from the X-ray structure of 2-benzoylpyrrole [6], calculation leads to the value $M = 2 \times \mu_b$(*N*-methylpyrrole) cos 55° + μ_b($Ph_2C{=}O$) = (2 × 1.95) cos 55° + 3.00 = 5.2 D close to the observed moment (5.11 ± 0.05 D), indicating that the Δm_s term can be ignored. Such a result does not imply that (2-pyrryl-carbonyl) and (phenyl-carbonyl) conjugation effects are similar because the lengths (l^* and l) of the transfer dipoles $\mathbf{m}^*$ and $\mathbf{m}$ may differ in the sense $l^* < l$ [19], and the m($Ph_2C{=}O$) mesomeric moment is calculated to be small since μ(benzophenone) — μ(dimesitylketone) = 2.98[23] — 2.84[23] = 0.14 D, only.

Let us now consider the specific solvent effect on the dipole moment of 2-benzoylpyrrole as a solute in weakly basic benzene and dioxane, and its incidence on the m^* value. For a closed-ring 2-acylpyrrole (2-ethyl-4,5-dihydro-3-methyl-indol-7(6H)-one, shown in Fig. 1), the large solvent effects (μ_b = 2.22 and μ_d = 2.74 D, as against μ_c = 1.55 ± 0.10 D) are indicative of an increase of 0.4 or 1.1 D in the (residue-carbonyl) mesomeric moment [4]. Such high increases in the m term are unlikely to apply to 2-benzoylpyrrole because, here, competition of (2-pyrryl-carbonyl) and (phenyl-carbonyl) conjugation effects tends to reduce the value of m^* to which this solvent effect is related. Also, for 2-benzoylpyrrole and di-(2-pyrryl)ketone, and their sulphur analogues, the dipole moment changes little on passing from the value in inert cyclohexane and/or carbon tetrachloride to that in benzene and dioxane (see Table 1). For these compounds the small increases in the dipole moments through the specific solvent effect are not due to a change in the conformational ratio as suggested by the following. The ϵ-dependent solvation effect, which is due to greater Onsager's reaction-field stabilization of the more polar conformer relative to the other(s) [24], should be similar in benzene and dioxane, and in cyclohexane and carbon tetrachloride, whose dielectric permittivities are close to each other, (2.26 and 2.20, 2.01 and 2.22 respectively; cf. the results for the conformational ratios for 2-formylfuran [25—27] and 2-formyl-*N*-methylpyrrole [3]). It then follows that, for 2-benzoylpyrrole, Δm_b can be taken as 0.1 D and Δm_d as 0.2 D, at the most. For 2-benzoylpyrrole as a solute in inert cyclohexane and carbon tetrachloride, and 2-benzoyl-*N*-methylpyrrole as a solute in benzene, the $\Delta \mathbf{m}_s$ term has been ignored. By so doing, calculation gives the M_s figures listed in Table 2.

The quadratic dipole moments of 2-benzoylpyrrole and 2-benzoyl-*N*-methylpyrrole can be quantified as

$$\mu_s^2 = x_s M_s^2(C) + (1 - x_s) M_s^2(T)$$

from which the following relative *C* populations (x_s) are derived: x_c = 0.91,

TABLE 2

Calculated dipole moments for retained conformers of 2-benzoylpyrrole, 2-benzoyl-*N*-methylpyrrole and their sulphur analogues (Debye units)

Conformer[a]	M_c	M_t	M_b	M_d
2-Benzoylpyrrole as *C*	1.28	1.29	1.28	1.19
2-Benzoylpyrrole as *T*	4.25	4.31	4.39	4.69
2-Benzoyl-*N*-methylpyrrole as *C*	—	—	1.09	—
2-Benzoyl-*N*-methylpyrrole as *T*	—	—	4.43	—
2-Thiobenzoylpyrrole as *C*	—	1.12	1.14	1.00
2-Thiobenzoylpyrrole as *T*	—	4.15	4.22	4.51
2-Thiobenzoyl-*N*-methylpyrrole as *C*	—	—	0.95	—
2-Thiobenzoyl-*N*-methylpyrrole as *T*	—	—	4.30	—

[a] See Fig. 1.

x_t = 0.88, x_b = 0.89 and x_d = 0.88 for the former, and x_b = 0.83 for the latter.

Cheng et al. [5] have suggested that 2-benzoylpyrrole as a solute in cyclohexane only exists in a nonplanar *C* form with the phenyl group rotated by 55 ± 10°, but this result from a Kerr constant study can be questioned since it is based on too low a value (1.27 D for $_EP + _AP = R_D$, as against our 1.76 D value) for the cyclohexane dipole moment; see Experimental.

Although 2-benzoylpyrrole as *C*, unlike 2-benzoyl-*N*-methylpyrrole in the same form, is stabilized by an intramolecular N—H•••O=C hydrogen bond its *C* population is only 0.1 units greater. This emphasizes the role played by Keesom dipole—dipole potentials in determining the preferred conformation of these compounds. Clearly, the dipole—dipole potential (between R—N and C=O dipoles) is much more attractive for the *C* models; a precise calculation of *U*(*C*) and *U*(*T*) potentials is not possible because the R—N moments are not known here*, but the *U*(*C*)/*U*(*T*) ratio can be roughly evaluated to 4. There is no doubt, however, that μ(Me—N(sp^2)) is 0.4 D less than μ(H—N(sp^2)) and, therefore, the *U*(*C*) — *U*(*T*) value favours 2-benzoyl-*N*-methylpyrrole as *C* less.

*The solution-state conformations of 2-thiobenzoylpyrrole and 2-thiobenzoyl-*N*-methylpyrrole*

As for the corresponding ketones, the more stable conformers (*C* and *T*) for 2-thiobenzoylpyrrole and 2-thiobenzoyl-*N*-methylpyrrole have their

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*These H—N and Me—N moments cannot be equated to the classical values (1.25 and 0.86 D) drawn from the dipole moments of ammonia (1.41 D [28]) and trimethylamine (0.86 D [29]) because they do not contain a term due to contribution of the nitrogen hybridization moment [30] which (if assumed to equal half the lone-pair moment [30]) is 1.78 [30] or 0.5 D [31] for tetrahedral nitrogen, and 1.77 [30] or 0.55 D [31] for trigonal nitrogen.

(2-pyrryl-thiocarbonyl) residue uniplanar and their phenyl group rotated by a finite ϕ' angle. Conjugation energies for (2-pyrryl-thiocarbonyl) and (phenyl-thiocarbonyl) groups are not known, but their values are likely to be markedly greater than those for the corresponding carbonyl groups, 52.2 [12] or 53 kJ mol^{-1} [13] for 2-formyl-*N*-methylpyrrole and 27 kJ mol^{-1} for benzaldehyde [14] because of what follows. As indicated by the $\mu(Ph_2C{=}Y) - \mu(Me_2C{=}Y)$ differences, the mesomeric moments of thiobenzophenone and benzophenone are 2.86 − 2.41 = 0.45 D [11] and 3.00[9] − 2.78[32] = 0.22 D, respectively [11]. On passing from thioacetone to thiobenzophenone, 2-thiobenzoylpyrrole or 2-thiobenzoyl-*N*-methylpyrrole the thiocarbonyl stretching frequency decreases from 1271 (CCl_4) to 1210 (KBr), 1105 (KBr) or 1100 cm^{-1} (KBr), whereas for the corresponding ketones the carbonyl stretching frequency passes from 1719 (CCl_4) to 1660 (CCl_4), 1630 (benzene) or 1636 cm^{-1} (CCl_4). (See Andrieu and Mollier [33] for the location of thiocarbonyl stretching frequencies.)

Assuming the phenyl-group rotational angle in both *C* and *T* conformers to be similar to the value (+ and −37.5°) in conrotatory thiobenzophenone [34], the dipole moments of 2-thiobenzoylpyrrole and 2-thiobenzoyl-*N*-methylpyrrole can be calculated by writing

$$\mathbf{M}'_s = \mu_b(Ph_2C{=}S) + \mu_s(\text{pyrrole or } N\text{-methylpyrrole}) + \Delta\mathbf{m}'_s \qquad (2)$$

where the $\Delta\mathbf{m}'_s$ vector is defined in the same way as $\Delta\mathbf{m}_s$ in eqn. (1).

Taking as before $\Delta m'_s$ = 0, 0.1 and 0.2 D for 2-thiobenzoylpyrrole in carbon tetrachloride, benzene and dioxane respectively, and $\Delta m'_b = 0$ for 2-thiobenzoyl-*N*-methylpyrrole in benzene, calculation yields the $\mathbf{M}'_s$ values indicated in Table 2.

Comparison of the experimental dipole moments with these calculated $M'_s(C)$ and $M'_s(T)$ values provides the following *C* populations: $x'_t = 0.73$, $x'_b = 0.66$ and $x'_d = 0.71$ for 2-thiobenzoylpyrrole in the specified solvent, and $x'_b = 0.64$ for 2-thiobenzoyl-*N*-methylpyrrole in benzene.

Interestingly, the *C* population for 2-thiobenzoylpyrrole is significantly lower than for 2-benzoylpyrrole, 0.7 as against 0.9; this is also observed for 2-thiobenzoyl-*N*-methylpyrrole ($x'_b = 0.65$) and 2-benzoylpyrrole ($x_b = 0.83$). These facts can be explained as follows: 2-thiobenzoylpyrrole as *C*, unlike 2-benzoylpyrrole in the same form, does not contain an intramolecular N—H···Y=C hydrogen bond. For both sulphur compounds the $U(C) - U(T)$ value should be markedly smaller than the one for the corresponding ketones because the C=S bond moment is much lower than the C=O value, as indicated by the dipole moments of gaseous thioformaldehyde (1.65 D [35]) and formaldehyde (2.34 D [36]). Greater steric interference in the *C* forms, especially for thiobenzoyl-*N*-methylpyrrole, may also play a role.

The solution-state conformations of di-(2-pyrryl)ketone and di-(2-N-methylpyrryl)ketone

As the (2-pyrryl-carbonyl) residue is uniplanar in 2-benzoylpyrrole as *C* [6], only the *cc* conformer for di-(2-pyrryl)ketone and di-(2-*N*-methylpyrryl)ketone can be regarded as nearly uniplanar. In the mixed conformers (*ct* and *tc*) a rotation of 45° probably occurs for one of the 2-pyrryl groups, and the *tt* conformer probably exhibits a conrotatory model similar to that of benzophenone [21], with $\phi' = -\phi'' = 30°$ (Fig. 2).

Interestingly, the carbonyl stretching frequency decreases more on passing from acetone (1719 cm^{-1}, CCl_4) to di-(2-pyrryl)ketone (1591, CCl_4) or di-(2-*N*-methylpyrryl)ketone (1619, CCl_4) than on going from acetone to benzophenone (1660, CCl_4). The experimental refraction (R_D) of di-(2-*N*-methylpyrryl)ketone (58.9 [15]) is 3.2 cm^3 higher than the value calculated from those of benzophenone (56.7 [16]), *N*-methylpyrrole (25.7 [18]) and benzene (26.2).

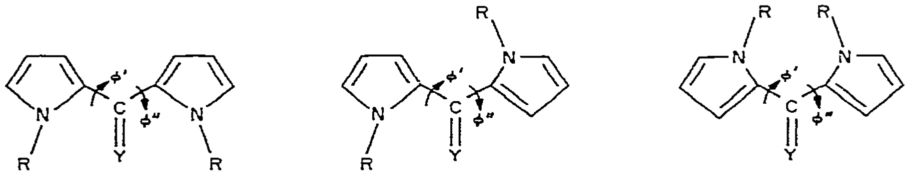
The dipole moments of di-(2-pyrryl)ketone and di-(2-*N*-methylpyrryl)ketone *cc*, *ct* and *tc*, and *tt* conformers can be calculated from the vectorial equations

$$\mathbf{M}_s = \mu_s(\mathrm{Ph_2C{=}O}) + \mu_s' + \mu_s'' + \Delta\mathbf{M}_s \qquad (3)$$

where $\mu_s' = \mu_s'' = \mu_s$(pyrrole or *N*-methylpyrrole) and $\Delta\mathbf{M}_s$ is the resultant along the carbonyl bond axis of the $\Delta\mathbf{m}_s$ vectors as defined in eqn. (1).

The ΔM_t term can be ignored, as shown by examination of the dipole moment in benzene of 1,1'-methylene-2,2'-dipyrrylketone (see p. 88), and plausible values for ΔM_b and ΔM_d are 0.15 and 0.30 D respectively. With these assumptions, calculation gives the M_s values listed in Table 3. CNDO/2 calculated moments for 2-benzoylpyrrole uniplanar *cc*, *ct*, *tc*, and *tt* conformers are 0.55, 3.35 and 3.35, and 5.93 D.

As 2-benzoylpyrrole and 2-benzoyl-*N*-methylpyrrole principally exist in the *C* conformation (x_s = 0.9 and 0.8), the *tt* conformer for di-(2-pyrryl)ketone and di-(2-*N*-methylpyrryl)ketone can be discarded; if assuming the relative stabilities of conformers determined by Keesom potentials between R—N and C=O dipoles*, then (*tt*) would be $(T)^2 = (0.1 \text{ or } 0.2)^2$ only.



cc (φ'=φ''=0°) *ct* (φ'=0°, φ''=45°) *tt* (φ'=φ''=30°)

Fig. 2. Retained conformers for di-(2-pyrryl)ketone and di-(2-*N*-methylpyrryl)ketone and their sulphur analogues. (φ' and φ'' angles are measured from the indicated uniplanar conformations.)

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*If so, $u(cc) = 2U(C)$, $u(ct) = u(tc) = U(C) + U(T)$, $u(tt) = 2U(T)$, and $(tt) = \exp[-u(tt)]/\{\exp[-u(cc) + 2\exp[-u(ct)] + \exp[-u(tt)]\} = \{\exp[-u(T)/\exp[-u(C)] + \exp[-u(T)]\}^2 = (T)^2$, where u stands for U/RT; similarly, $(cc) = (C)^2$, $(ct) = (tc) = (C)\cdot(T)$. (Cf. [37]). This only holds for uniplanar models.

TABLE 3

Calculated dipole moments for retained conformers of di-(2-pyrryl)ketone, di-(2-*N*-methylpyrryl)ketone and their sulphur analogues (Debye units)[a]

Conformer[b]	M_c	M_t	M_b	M_d
Di-(2-pyrryl)ketone as *cc*	—	0.49	0.51	0.80
Di-(2-pyrryl)ketone as *ct*	—	2.59	2.72	2.93
Di-(2-pyrryl)ketone as *tt*	—	4.71	4.90	5.34
Di-(2-*N*-methylpyrryl)ketone as *cc*	—	—	0.87	—
Di-(2-*N*-methylpyrryl)ketone as *ct*	—	—	2.65	—
Di-(2-*N*-methylpyrryl)ketone as *tt*	—	—	4.85	—
Di-(2-pyrryl)thioketone as *cc*	0.60	0.66	0.65	1.00
Di-(2-pyrryl)thioketone as *ct*	2.48	2.50	2.62	2.80
Di-(2-pyrryl)thioketone as *tt*	4.52	4.54	4.76	5.15
Di-(2-*N*-methylpyrryl)thioketone as *cc*	—	—	1.01	—
Di-(2-*N*-methylpyrryl)thioketone as *ct*	—	—	2.56	—
Di-(2-*N*-methylpyrryl)thioketone as *tt*	—	—	4.72	—

[a] Models for conformers are described in text and Fig. 2. [b] $M(tc) = M(ct)$.

Examination of CNDO/2 calculated total energies of uniplanar di-(2-pyrryl)-ketone conformers, though inaccurate, clearly allows exclusion of the *tt* conformer since, as compared to the value of the *cc* form, these energies are 16.6 kJ mol^{-1} for mixed conformers (*ct* and *tc*) and as high as 277 kJ mol^{-1} for the *tt* conformer. It then follows that the quadratic dipole moments of di-(2-pyrryl)ketone and di-(2-*N*-methylpyrryl)ketone can be quantified as

$$\mu_s^2 = X_s \cdot M_s^2(cc) + Y_s' \cdot M_s^2(ct) + Y_s'' \cdot M_s^2(tc) = X_s \cdot M_s^2(cc) + Y_s \cdot M_s^2(ct)$$

where X_s designates the *cc* population and Y_s the total population in mixed forms ($Y_s = Y_s' + Y_s''$).

From the dipole moments of di-(2-pyrryl)ketone and di-(2-*N*-methylpyrryl)ketone listed in Table 1, one readily calculates $X_t = 0.92$, $X_b = 0.88$ and $X_d = 0.92$, and $X_b = 0.94$, respectively. With the CNDO/2 calculated values for the *cc* and mixed conformers of di-(2-pyrryl)ketone, an X_t of 0.96 is derived.

Although di-(2-*N*-methylpyrryl)ketone, as *cc* and mixed, is not stabilized by two (or one) intramolecular H—H···O=C bond (contrary to the same forms of di-(2-pyrryl)ketone), its X_s value is similar. This fact emphasizes the role played by dipole-dipole potentials in determining the preferred conformation of these compounds.

*The solution-state conformations of di-(2-pyrryl)thioketone and di-(2-*N*-methylpyrryl)thioketone*

Retained conformers for di-(2-pyrryl)thioketone and di-(2-*N*-methylpyrryl)thioketone are similar to those assumed for the corresponding ketones (Fig. 2).

The thiocarbonyl stretching frequency augments more on passing from thioacetone (1271 cm^{-1}, CCl_4) to di-(2-pyrryl)thioketone (1097, KBr) or di-(2-*N*-methylpyrryl)thioketone (1094, KBr) than on going from thioacetone to thiobenzophenone (1210, KBr). The decrements (174, 177 and 61 cm^{-1}) are higher than those for the corresponding ketones, 120, 100 and 59 cm^{-1}, indicating that the (arene—thiocarbonyl) conjugation is greater than the (arene—carbonyl) conjugation [11].

The dipole moments of the conformers may be calculated by using the vectorial equations

$$\mathbf{M}'_s = \mu_b(\mathrm{Ph_2C{=}S}) + \mu'_s + \mu''_s + \Delta \mathbf{M}'_s \qquad (4)$$

where μ'_s, μ''_s and $\Delta\mathbf{M}'_s$ have the same meaning as in eqn. (3).

Assuming, as before, $\Delta M'_c = \Delta M'_t = 0$, $\Delta M'_b = 0.15$ D and $\Delta M'_d = 0.3$ D for di-(2-pyrryl)thioketone, and $\Delta M'_b = 0$ for di-(2-*N*-methylpyrryl)thioketone, calculation leads to the M'_s values given in Table 3. CNDO/2 calculated dipole moments for uniplanar *cc*, *ct*, *tc* and *tt* conformers are 0.82, 2.98, 2.98 and 5.34 D.

As for the corresponding ketones the *tt* conformer can be precluded for di-(2-pyrryl)thioketone and di-(2-*N*-methylpyrryl)thioketone. CNDO/2 calculated energies for the mixed and *tt* conformers are 21 and 286 kJ mol^{-1} above that of the *cc* conformer.

The *cc* populations for di-(2-pyrryl)thioketone and di-(2-*N*-methylpyrryl)thioketone can then be calculated from their experimental dipole moments listed in Table 1, $X'_c = 0.69$, $X'_t = 0.62$, $X'_b = 0.65$ and $X'_d = 0.71$, and $X'_b = 0.46$, respectively. By using the CNDO/2 calculated values for the *cc* and mixed conformers, X'_c becomes 0.82 and X'_t 0.76.

Greater steric interference in the *cc* conformer probably explains why the *cc* population is markedly lower for di-(2-*N*-methylpyrryl)thioketone than for the corresponding ketone, 0.5 as against 0.9.

The *cc* population for di-(2-pyrryl)thioketone ($X'_s = 0.7$) is lower than the one for di-(2-pyrryl)ketone ($X_s = 0.9$) because the former does not contain an intramolecular N—H···Y=C hydrogen bond, and also because the $U(C) - U(T)$ value is smaller (see p. 90).

CONCLUSIONS

The main conclusions that can be drawn from this study are the following.

Like 2-formylpyrrole and 2-acetylpyrrole [1—4], 2-benzoylpyrrole and 2-benzoyl-*N*-methylpyrrole, as solutes in nonpolar media, principally exist in the *cis* conformation with $(C) = 0.9$ and 0.8 respectively; an intramolecular N—H···O=C hydrogen bond in the former as *C* explains why the *C* population is greater.

2-Thiobenzoylpyrrole and 2-thiobenzoyl-*N*-methylpyrrole also exist mostly in the *cis* conformation, with a similar value (0.7) for the *C* population, probably because the former as *C* is not stabilized by an intramolecular N—H···S=C hydrogen bond.

As expected from these results, di-(2-pyrryl)ketone and di-(2-*N*-methylpyrryl)ketone mainly exist in the $(\textit{cis})_2$ conformation, with (*cc*) = 0.9 for both of them despite existence in the former as *cc* of two (bifurcated) N—H···O=C hydrogen bonds. Other stable conformers are *ct* and *tc*, as the *tt* conformer can be discarded because of its excessively high CNDO/2 calculated energy, compared to that of the *cc* and mixed conformers.

2-Thiobenzoylpyrrole, which is not stabilized (as *cc* and mixed) by two (or one) N—H···S=C hydrogen bond(s), also prefers to exist as $(\textit{cis})_2$ [(*cc*) = 0.7] while 2-thiobenzoyl-*N*-methylpyrrole, which as *cc* is more sterically crowded, is an equimolecular mixture of *cc* and mixed-forms.

The fact that the conformational ratio is similar for 2-benzoylpyrrole and 2-benzoyl-*N*-methylpyrrole, di-(2-pyrryl)ketone and di-(2-*N*-methylpyrryl)ketone, emphasizes the role played by dipole—dipole potentials in determining the preferred conformations of these compounds.

EXPERIMENTAL

Materials

R.P. Normapur cyclohexane (analytical reagent), carbon tetrachloride for spectrometry, R.P. Normapur benzene (for cryoscopy) and R.P. Normapur dioxane (analytical reagent), all from Prolabo (Paris), were purified by standard methods [38]. Cyclohexane and carbon tetrachloride were redistilled and dried over molecular sieves (3 Å); benzene and dioxane were recrystallized and dried over metallic sodium, and by molecular sieves. At 30.0°C, they presented the physical constants (d_4 and ϵ, dielectric permittivity): 0.7694, 2.0113; 1.5748, 2.2208; 0.8687, 2.2642, 1.0227, 2.2055 (ϵ values are referred to that of benzene as 25.0°C, taken as 2.2741).

2-Benzoylpyrrole was prepared as indicated in ref. 39: m.p. 75°C (lit. 77—78°C [39]); IR spectrum (KBr), 3288, 1629 cm^{-1} (ν_s(C=O)); ^{1}H NMR spectrum ($CDCl_3$), 6.18q(1H), 6.70q(1H), 6.97q(1H), 7.30m(3H), 7.75q(2H), 10.32ls(1H)*.

2-Benzoyl-*N*-methylpyrrole was also obtained after ref. 39: b.p. 115—120°C/0.5 torr; IR spectrum (KBr), 3100, 2942, 1625 cm^{-1} (ν_s(C=O)); ^{1}H NMR spectrum ($CDCl_3$), 4.05s(3H), 6.12q(1H), 6.60q(1H), 6.90q(1H), 7.40m(3H), 7.78m(2H).

2-Thiobenzoylpyrrole (I) and 2-thiobenzoyl-*N*-methylpyrrole (II), not described before, were prepared as follows.

To a stirred solution of the corresponding ketone (1 g) in dry benzene (80 cm^3) was added P_4S_{10} (2 g). The mixture was allowed to stand in an ultrasonic bath for two hours. After removal of the excess of P_4S_{10} by filtration, the solid residue was dissolved in ethyl acetate—petroleum ether (1:3) and the solution chromatographed on silica gel. The operation is re-

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*s, ls, q and m stand for singlet, large singlet, quartet and multiplet, respectively.

peated if the compounds are not pure. I and II are red liquids characterized as indicated hereafter.

I: IR spectrum (KBr), 3360, 1520, 1400, 1380, 1255, 1220, 1097 (ν_s-(C=S)), 1048, 1032 cm^{-1}; ^{1}H NMR spectrum (CDCl$_3$), 6.32m(1H), 6.59m(1H), 7.2—7.8m(6H), 9.70ls(1H).

II: IR spectrum (KBr), 3062, 2960, 1450, 1390, 1360, 1330, 1235, 1175, 1094 (ν_s(C=S)), 1060, 1045 cm^{-1}; ^{1}H NMR spectrum (CDCl$_3$), 4.12s(3H), 6.20q(1H), 6.65q(1H), 7.2—7.8m(6H).

Di-(2-pyrryl)ketone was prepared as recommended in refs. 40 and 22: m.p. 158°C (lit. 158—159°C [22]); IR spectrum (KBr), 3420, 3372, 1572 cm^{-1} (ν_s(C=O)); ^{1}H NMR spectrum (CDCl$_3$), 6.26q, 6.90m(2H), 7.02m(2H), 9.70ls(2H).

Di-(2-*N*-methylpyrryl)ketone was obtained after 22: m.p. 25°C (lit. 25—26°C [22]); IR spectrum (KBr), 3310, 1600 (ν_s(C=O)), 1528 cm^{-1}; ^{1}H NMR spectrum (CDCl$_3$), 3.88s(6H), 6.00q(2H), 6.72m(4H).

Di-(2-pyrryl)thioketone was prepared as indicated in refs. 40 and 22: m.p. 98°C (lit. 96—98°C [22]); IR spectrum (KBr), 3401, 1522, 1400, 1097 (ν_s(C=S)), 1062 cm^{-1}; ^{1}H NMR spectrum (CDCl$_3$), 6.35m(2H), 6.97m(2H), 7.22m(2H), 1013ls(2H).

Di-(2-*N*-methylpyrryl)thioketone was obtained as recommended in ref. 22: m.p. 100°C (lit. 100—101°C [22]); IR spectrum (KBr), 1450, 1395, 1310, 1230, 1094 (ν_s(C=S)), 1046, 1026 cm^{-1}; ^{1}H NMR spectrum (CDCl$_3$), 4.13s(6H), 6.29q(2H), 6.73q(2H), 7.10m(2H).

1,1′-Methylene-2,2′-dipyrrylketone (m.p. 162—164°C) was donated by Pr. Dr. J. Lugtenburg [22].

Physical measurements

The IR spectra were recorded on a Perkin-Elmer 225 spectrometer, and ^{1}H NMR spectra on a Varian EM-360 spectrometer (frequency 60 MHz).

The electric dipole moments were measured in the specified solvent at 30.0°C using the well-known Debye refractivity method. The total polarization of the solute, extrapolated to infinite dilution, was calculated from the experimental ratios [41]

$$\alpha_0 = \lim_{(w=0)} [(\epsilon - \epsilon_1)/w] \text{ and } \beta = \Sigma(v - v_1)/\Sigma w$$

where w is the weight fraction of the solute, ϵ and v are the dielectric permittivity and specific volume of the solutions respectively, and subscript one refers to the pure solvent as used, i.e., made up in the same way as the solutions. The α_0 value was calculated from the linear function, $\alpha = \alpha_0 + \alpha' w$, obtained by least-squares analysis of the $\epsilon(w)$ polynomial (quadratic) function.

The distortion polarization of the solute, ${}_E P + {}_A P$, was assumed to equal the molecular refraction (R_D) calculated by additivity from the experimental refractions of 2-benzoyl-*N*-methylpyrrole (57.7 cm^3 [15]) or di-(2-*N*-methylpyrryl)ketone (58.9 [15]), *N*-methylpyrrole (25.7 [18]), pyrrole (20.7 [42]) and benzene (26.2), and the differences between (C=S) and (C=O) bond increments (11.91 — 3.32 = 8.59 cm^3 [17]). The experimental refractions of 2-benzoylpyrrole, 2-benzoyl-*N*-methylpyrrole, di-(2-pyrryl)-ketone and di-(2-*N*-methylpyrryl)ketone were found to be in accord, within 0.5 cm^3, with the values calculated by additivity. For the sake of homogeneity, the latter were used in experimental dipole-moment calculations.

Infrared spectroscopy shows that 2-benzoylpyrrole and di-(2-pyrryl)-ketone are partly dimerized in CCl_4 solution. The high values found for $B_0 = (\partial p_2/\partial w)_0$ (p_2 is the specific polarization of the solute), to which the dimerization constant K is simply related [43]*, is indicative of association for 2-benzoylpyrrole in cyclohexane ($B_0 = -24.3$ cm^3 g^{-1}) and carbon tetrachloride ($B_0 = -19.1$), and for di-(2-pyrryl)ketone in carbon tetrachloride ($B_0 = +21.3$). It results from these facts that, to obtain an accurate value for the dipole moments of these weakly acidic compounds in an inert, non-basic solvent, a large number of very dilute solutions must be carefully examined. Thus, for 2-benzoylpyrrole in cyclohexane solution, the extrapolated α_0 value from 25 solutions whose solute weight fraction lay between 0.001 and 0.003 is 1.9, while the α_0 term as deduced from examination of more concentrated solutions ($0.005 < w < 0.020$) is 1.3, only, from which too a low dipole moment is deduced, 1.5 D as against 1.76 D from $\alpha_0 = 1.9$. Cheng et al.'s dipole moment for 2-benzoylpyrrole in cyclohexane (1.27 D [5], for ${}_EP + {}_AP = R_D$) may be due to the fact that Authors have not examined sufficiently dilute solutions.

In dioxane, and to a lesser extent in benzene, 2-benzoylpyrrole and di-(2-pyrryl)ketone form hydrogen-bonded complexes with the weakly basic solvent, and this much lowers self-association of the solute and makes the α' slope negligibly small.

Interestingly, 2-thiobenzoylpyrrole and di-(2-pyrryl)thioketone are not partly dimerized in inert solvents, such as cyclohexane and carbon tetrachloride. This fact is probably due to relatively weak basic character of thioketones as compared to ketones; formation constants (in CCl_4) for *p*-chlorophenol···thiocamphor and *p*-chlorophenol···camphor hydrogen-bonded complexes are 1.5—2.0 and 21.8 M^{-1}, respectively [44].

The techniques used for the measurement of dielectric permittivities, specific volumes and refraction indices are described elsewhere [45, 46].

For each solute, the maximum value of w (w_{max}), given to only three decimal places (though it is known to five to six), α_0, β (cm^3 g^{-1}), $P_{2\infty}$ and R_D (both in cm^3 mol^{-1}) and μ (in Debye units) are given in Table 4.

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*$K_s = \{(9kT/4\pi N) \cdot (M_2^2/M_s) \cdot B_0)\}/(\mu'^2 - 2\mu^2)$, where M_2 and M_s are the molecular weights of the solute and solvent, μ' and μ the dipole moments of the monomer and dimer. For 2-benzoylpyrrole, K_c/K_t is calculated to be 2.3, and K_c results as 5.8 M^{-1} if assuming $\mu' = 0$. (In ref. 43, p. 282, in the expression for B_0, read $\alpha_0 \beta(\epsilon_1 + 2)$; 1 Debye (D) = $(0.2998)^{-1} \times 10^{-30}$ C m; p. 284, $\mu_s = \mu_g[1 - C(\epsilon_s - 1)^2]$.)

TABLE 4

Physical data from dipole moment determinations at 30.0°C

Solute	s	w_{max}	α_0	$-\beta$	$P_{2\infty}$	R_D	μ(D)
2-Benzoylpyrrole	c	0.003	1.9[a]	0.461	115.0	52.7	1.76 ± 0.07[b]
2-Benzoylpyrrole	t	0.007	4.5[c]	—0.204	126.0	52.7	1.91 ± 0.03
2-Benzoylpyrrole	b	0.013	2.50	0.312	123.9	52.7	1.88 ± 0.01
2-Benzoylpyrrole	d	0.018	3.10	0.139	129.2	52.7	1.95 ± 0.02
2-Thiobenzoylpyrrole	t	0.009	6.50	—0.181	174.3	61.3	2.37 ± 0.02
2-Thiobenzoylpyrrole	b	0.023	4.35	0.335	200.0	61.3	2.63 ± 0.02
2-Thiobenzoylpyrrole	d	0.005	4.85	0.162	194.3	61.3	2.57 ± 0.04
2-Benzoyl-*N*-methylpyrrole	b	0.014	2.75	0.275	144.9	57.7	2.08 ± 0.02
2-Thiobenzoyl-*N*-methylpyrrole	b	0.008	4.25	0.295	213.6	66.3	2.70 ± 0.02
Di-(2-pyrryl)ketone	t	0.003	1.6[d]	—0.166	64.2	48.9	0.87 ± 0.03
Di-(2-pyrryl)ketone	b	0.011	1.10	0.350	71.5	48.9	1.06 ± 0.02
Di-(2-pyrryl)ketone	d	0.008	1.50	0.195	75.8	48.9	1.16 ± 0.02
Di-(2-pyrryl)thioketone	c	0.004	1.5	0.480	100.5	57.5	1.46 ± 0.03
Di-(2-pyrryl)thioketone	t	0.005	3.64	—0.185	110.4	57.5	1.62 ± 0.02
Di-(2-pyrryl)thioketone	b	0.013	2.03	0.331	110.7	57.5	1.63 ± 0.01
Di-(2-pyrryl)thioketone	d	0.009	2.60	0.158	117.4	57.5	1.73 ± 0.03
Di-(2-*N*-methylpyrryl)ketone	b	0.026	0.93	0.293	81.2	58.9	1.05 ± 0.01
Di-(2-*N*-methylpyrryl)thioketone	b	0.015	2.55	0.337	148.2	67.5	2.00 ± 0.02
1,1'-Methylene-2,2'-dipyrrylketone	b	0.008	16.5	0.410	577.4	52.1	5.11 ± 0.05

[a] $\alpha = 1.9 - 100\,w$. [b] Lit. $\mu = 1.27$ D if recalculated with authors' value for R_D [5]; see text for a possible cause of the discrepancy with our figure. [c] $\alpha = 4.5 - 175\,w$. [d] $\alpha = 1.6 + (\sim 200)\,w$.

CNDO/2 computations

Total energies and dipole moments were calculated for all uniplanar conformers of di-(2-pyrryl)ketone and di-(2-pyrryl)thioketone [47, 48]. The following interatomic distances and intervalency angles were used: C=O 1.213 Å, CC(=O)C 120.4° [49]; C—CO 1.48 Å [6], C=S 1.636 Å, CC(=S)C 117.3° [34], C_2—CS 1.50 Å; other dimensions from the microwave structure of pyrrole [50]. Calculations were performed by using standard programme CNINDO, with a 6600 CDC computer system [51]. Results for di-(2-pyrryl)ketone as *cc*, *ct* and *tt* respectively are E(au) = —111.61537, —111.60905, —111.50961, μ(D) = 0.55, 3.35, 5.93, and for di-(2-pyrryl)-thioketone E(au) = —104.16012, —104.15207, —104.05111, μ(D) = 0.82, 2.98, 5.34.

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