PREFERRED CONFORMATIONS OF METHYLTHIO-ACETONE AND -ACETOPHENONE, METHYLSULPHONYL-ACETONE AND -ACETOPHENONE, FROM MOLECULAR-MECHANICS AND DIPOLE-MOMENT TECHNIQUES

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ABSTRACT

Preferred conformations for the title compounds are determined from calculated molecularmechanics energies in the gaseous phase and analysis of the dipole moments measured in solvents of low dielectric permittivity, In all cases, the *gauche* conformer having the Me-S bond situated far away from the Me(-C) (or Ph(-C)) group, and nearly bisecting one of the C(=O)-C-Hvalleys, is predominant.

INTRODUCTION

In continuation of our preceding studies on α -substituted acetones by IR spectroscopy [1, 2], photoelectron and UV spectroscopies [3], and the dipole moment technique [4, 5], α -methylthio- and α -methylsulphonyl-acetone, ω -methylthio- and ω -methylsulphonyl-acetophenone are here examined by molecular mechanics and dipole moment techniques with the aim of determining their preferred conformations in the solution state.

MOLECULAR MECHANICS CALCULATIONS

Molecular-mechanics energies of $MeCOCH_2SMe$, $MeCOCH_2SO_2Me$, Ph-COCH₂SMe and PhCOCH₂SO₂Me conformers were computed by means of the

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TABLE 1

Parameters used in molecular-mechanics calculations on McCOCH₂SO₂Me and PhCOCH₂SO₂Me^a

Bond	$k_{\rm s}$ (mdyn Å ⁻¹)	$l_{\rm o}$ (Å)	Intervalency angle	$k_{ m b}$ (mdyn Å rad ⁻¹)	$ heta_{ m o}$ (degrees)
S=0	6.5	1.450	C(Me)-S=O	0.350	109.0
			0=S=0	0.350	118.0
			C(=0)-C-S	0.500	110.0
			H-C-S	0.510	108.6
Dihedral angle		V_1		V ₂	V_3
		(k	cal mol ^{-1})	$(kcal mol^{-1})$	(kcal mol ⁻¹ $)$
S-C-C=	=0	0.0	000	0.000	0.000
S-C-C	(=O)-C(Me)	0.0	000	0.000	0.000
S-C-C	$(=0)-C_{ar}$	0.0	000	0.000	0.000
H-C-S-	-C	0.0	000	0.000	0.500
C(=0)-	-C-S-C	0.0	000	0.000	0.500
C(=0)-	-C-S=0	0.0	000	0.000	0.500
H-C-S=O		0.000		0.000	0.280

^aSee Fig. 1.

MM2 computer program [6], run on an IBM-PC/XT compatible machine. For the $-SO_{2^-}$ group the relevant parameters (listed in Table 1) were estimated from normal coordinate analysis of dimethyl sulphone by means of the GF matrix method of Wilson et al. [7]; the S=O bond moment was taken as 2.8 D [8]. Further, it has been assumed that $k_s = 7.0$ mdyn Å⁻¹ and $l_0 = 1.397$ Å for the $C_{ar}-C_{ar}$ bond in the phenyl ring of the acetophenones.

EXPERIMENTAL

Sample preparation

R.P. Normapur n-hexane (analytical reagent), carbon tetrachloride (for spectroscopy) and benzene (for cryoscopy), all from Prolabo (Paris), were distilled and dried with molecular sieves (3 Å) and (with the exception of CCl_4) metallic sodium; at 30.0°C they gave the physical constants d_4 and ϵ (the dielectric permittivity referred to that of benzene at 25.0°C taken as 2.2741) as follows: n-hexane, 0.6512 and 1.8750; carbon tetrachloride, 1.5748 and 2.2208; benzene, 0.8687 and 2.2642.

Methyl n-propyl sulphide (n-PrSMe), a commercial product (from Columbia Organic Chemicals, Inc., Columbia, SC, U.S.A.), was redistilled and dried with molecular sieves: b.p. 96°C; at 20.0°C, d_4 =0.8425 and n_D =1.4440 (literature values: 95.47°C, 0.8424 and 1.44435 [9]).

Methylthioacetone (MeCOCH₂SMe) was prepared according to Bradsher et al. [10]: b.p. 152°C, $n_{\rm D}$ = 1.4715 at 25.0°C (cf. 152.5–153°C and 1.4713 [10]).

Ethylthioacetone (MeCOCH₂SEt) was obtained as indicated by Bergson and Delin [11]: b.p. 170° C (literature value: 168–172°C [11]).

 ω -Methylthioacetophenone (PhCOCH₂SMe) was prepared following the same method as that given for ω -ethylthioacetophenone [12]: b.p. 86°C at 0.5 mm Hg (cf. 102–104°C at 2 mm Hg [13], 119–120°C at 5 mm Hg [14]); $n_{\rm D}$ =1.5835 at 20.0°C (literature value: 1.5836 [13]).

Methylsulphonylacetone (MeCOCH₂SO₂Me), m.p. $50-52^{\circ}$ C (cf. 54° C [12]), and ω -methylsulphonylacetophenone (PhCOCH₂SO₂Me), m.p. 110° C (literature value: 111° C [14]), were prepared from an adaptation of the method described for the oxidation of some alkyl- and aryl-sulphides [15], i.e. from the reaction of the β -ketosulphide (0.001 mol) with a methanolic solution of hydrogen peroxide (0.005 mol) and selenium dioxide (0.001 mol), below room temperature.

All compounds were analyzed by GLC to assess their purity.

Physical measurements

The electric dipole moments were determined in the specified solvent (n-hexane, h; carbon tetrachloride, t; or benzene, b) at 30.00 ± 0.02 °C by using the well-known Debye refractivity method. The total polarization of the solute, extrapolated to infinite dilution, was calculated from the experimental ratios α_0 and β defined as [16]

$$\alpha_0 = \lim_{w=o} \left[\frac{\epsilon - \epsilon_1}{w} \right]$$

and

$$\beta = \sum (v - v_1) / \sum w$$

where w is the weight fraction of the solute, ϵ and v are the dielectric permittivity and specific volume of the solutions, 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, $_{\rm E}P + _{\rm A}P$, was assumed to be equal to the molar refraction for the sodium D-line ($R_{\rm D}$). The value measured on the pure liquids was adopted for n-PrSMe (28.5) and MeCOCH₂SEt (33.2 [17]). Molar refractions for MeCOCH₂SMe and PhCOCH₂SMe were deduced from that of MeCOCH₂SEt by using $R_{\rm D}$ (CH₂) = 4.647 [18] and $R_{\rm D}$ (PhCOMe) = 36.27 cm³ mol⁻¹ [19], and those for the corresponding sulphones by adding $R_{\rm D}$ (n-PrSO₂Me) - $R_{\rm D}$ (n-PrSMe) = 0.86 [20] to the ones of MeCOCH₂SMe and PhCOCH₂SMe, respectively.

TABLE 2

Physical data from dipole moment determinations at 30.0°C in various solvents

Compound	Solvent ^a	w_{\max}	$lpha_{0}$	$-\beta$	$P_{2\infty}$	$R_{\rm D}$	μ(D)
n-PrSMe	 t	0.006	5.60	-0.571	85.5	28.4	1.68
n-PrSMe	b	0.038	2.60	-0.055	76.8	28.4	1.55
$MeCOCH_2SMe$	t	0.011	6.85	-0.348	105.9	28.6	1.96
MeCOCH ₂ SMe	b	0.057	4.53	0.168	120.0	28.6	2.13
MeCOCH ₂ SEt	t	0.031	5.56	-0.381	105.0	33.2	1.89
MeCOCH ₂ SEt	b	0.082	4.01	0.135	125.6	33.2	2.14
PhCOCH ₂ SMe	t	0.021	6.10	-0.235	150.3	49.0	2.24
PhCOCH ₂ SMe	h	0.033	2.31	0.675	150.1	49.0	2.23
MeCOCH ₂ SO ₂ Me	b	0.010	7.88	-0.394	234.3	29.4	3.19
PhCOCH ₂ SO ₂ Me	b	0.023	7.61	0.363	332.8	49.8	3.75

^at, Carbon tetrachloride; b, benzene; h, n-hexane.

The techniques used to determine the refraction index of the pure liquids and the dielectric permittivity and specific volume of the solvent and solutions have been described elsewhere [5,21].

For each solute, w_{max} (here reported to only three decimal places although it is known to five or six places), α_0 , β (in cm³ g⁻¹), $P_{2\infty}$ and R_D (both in cm³ mol⁻¹) and μ (in Debye units; 1 D=3.3356×10⁻³⁰ C m) are given in Table 2.

RESULTS AND DISCUSSION

Table 3 lists the molecular-mechanics energies and dipole moments for the minimum-energy conformations of $MeCOCH_2SMe$, $PhCOCH_2SMe$, $MeCOCH_2SO_2Me$ and $PhCOCH_2SO_2Me$. Calculated energies refer to the species as isolated, whereas dipole moments refer to the conformers (or compounds) in solution.

Calculated dipole moments for the minimum-energy conformers of Me-COCH₂SMe and MeCOCH₂SO₂Me were obtained from μ_b (EtCOMe) = 2.73 D [5], μ_t (EtCOMe) = 2.84 D [22], and μ_h (EtCOMe) = 2.84 D (cf. [5]), μ_b (n-PrSMe) = 1.55 D, μ_t (n-PrSMe) = 1.68 D (Table 1), μ_h (n-PrSMe) = 1.55 D (assumed), acting at -49.5° to the CH₂-S bond axis (from the Me₂S angle, 99.1° [23]), μ_b [(n-Pr)₂SO₂] = 4.47 D [24], acting at -51.7° to the CH₂-S link (from the Me₂SO₂ angle, 103.3° [25]), and the pertinent intervalency angles taken from the microwave structure of MeCOCH₂F existing as the *trans* form [26]*. The values for PhCOCH₂SMe and PhCOCH₂SO₂Me were calcu-

^{*}Note that n-PrSMe, like EtSMe and t-BuSMe ($\mu_b = 1.60$ [27] and 1.57 D [28]), exhibits a dipole moment markedly higher than that of Me₂S (1.45 D [28]). The dipole moments of RSO₂Me (with $R \neq Me$) are not known; the value for n-PrSO₂Me was taken as the one of (n-Pr)₂SO₂ (4.47 D [24]), and not of Me₂SO₂ (4.26 D [29]), from the fact that μ (n-PrSMe) differs from μ (Me₂S) by 0.10 D.

TABLE 3

Species	Conformer	$\psi,\phi^{ m b}$	Ε	μ (calc.)	$\mu(\exp.)$
MeCOCH ₂ SMe	I	109.6, - 65.0	0.724	1.28°,1.29 ^f	
MeCOCH ₂ SMe	11	109.5, 179.0	1.151	$3.28^{\circ}, 3.12^{f}$	
MeCOCH ₂ SMe	III	63.0, 65.0	2.509	3.94°,3.74 ^f	
MeCOCH ₂ SMe	Solute				1.96°,2.13 ^f
MeCOCH ₂ SEt	Solute				1.89 ^e ,2.14 ^f
MeCOCH ₂ SO ₂ Me	I' ^c	87.0, - 61.0	2.011	2.56^{f}	
MeCOCH ₂ SO ₂ Me	II' ^d	122.0, -176.0	3.261	4.76 ^f	
MeCOCH ₂ SO ₂ Me	Solute				3.19
PhCOCH ₂ SMe	Ι	103.5, -64.0	3.815	$1.60^{\circ}, 1.69^{g}$	
$PhCOCH_2SMe$	II	0.5, - 75.0	6.534	3.96°,3.86 ^g	
PhCOCH ₂ SMe	III	1.0, -179.5	6.714	4.62°,4.49 ^g	
$PhCOCH_2SMe$	Solute				$2.24^{\circ}, 2.25^{\rm g}$
$PhCOCH_2SO_2Me$	I'	96.0, - 60.0	5.520	2.42^{f}	
PhCOCH ₂ SO ₂ Me	II'	93.0, -178.0	7.320	$5.63^{\rm f}$	
PhCOCH ₂ SO ₂ Me	III′	5.0, - 63.0	7.615	5.90 ^f	
PhCOCH ₂ SO ₂ Me	IV'	83.0, 63.0	8.927	6.56^{f}	
PhCOCH ₂ SO ₂ Me	V′	2.0, 180.0	9.472	7.35^{f}	
PhCOCH ₂ SO ₂ Me	Solute				3.76^{f}

Calculated molecular-mechanics energies (kcal mol⁻¹) and electric dipole moments (Debye units)^a for the minimum-energy conformations of methylthio- and methylsulphonyl-acetone, ω -methylthio- and ω -methylsulphonyl-acetophenone

^aBy additivity as indicated in text. ^b ψ and ϕ rotational angles (in degrees) are defined in Fig. 1. ^{c,d} μ =2.243 and 4.757 D from the atomic net charges used in molecular-mechanics energy calculations. ^{e,f,g}In carbon tetrachloride, benzene and n-hexane, respectively.

lated using $\mu_{\rm h}({\rm PhCOMe}) = 2.97$ D, $\mu_{\rm t}({\rm PhCOMe}) = 2.97$ D or $\mu_{\rm b}({\rm PhCOMe}) = 2.95$ D (see ref. 5), acting at 50° to the Ph–CO bond axis [30], and the relevant intervalency angle taken from the X-ray structure of Ph-COCH₂I existing as *gauche* [31].

Preferred conformations of methylthio- and methylsulphonyl-acetone

The title compounds can exist in a number of conformations characterized by the dihedral angles $\psi = O = C - CH_2 - S$ and $\phi = Me - S - CH_2 - C(=O)$ (Figs. 1 and 2). Conformers with $\psi \leq 63^{\circ}$ will be regarded as *cis* (C), and those with $\psi > 90^{\circ}$ as gauche (G).

A choice among the conformers of methylthio- and methylsulphonyl-acetone can be made on the following comparative criteria: (a) no eclipsing of Me-S with H-C(3) (or C(2)-C(3)) bonds (cf. ref. 32); (b) no repulsive contact, or neighbouring, between the sulphur lone-pairs p(S) (or sulphonyl-oxygen atoms) and one of the lone-pairs of the carbonyl-oxygen atom (see ref.



Fig. 1. More unstable (0,0)-conformers of methylthioacetone (R=Me), ω -methylthioacetophenone (R=Ph), methylsulphonylacetone (R=Me) and ω -methylsulphonylacetophenone (R=Ph), characterized by $\psi = 0^\circ$, $\phi = 0^\circ$: p designates a sulphur lone-pair in the sulphur compounds.



Fig. 2. Newman projections of RCOCH₂SMe and RCOCH₂SO₂Me (R=Me or Ph; X=sulphur lone-pair or oxygen atom) indicating the ψ and ϕ rotational angles about the C(=O)-CH₂ and CH₂-S bond axis, respectively.

33), to be trigonally hybridized [34]; (c) no repulsive an der Waals neighbouring between Me(-S) and Me(-C(2)) groups*.

(1) From the calculated molecular-mechanics energies for the gauche conformers I and II, and cis-like conformer III, of MeCOCH₂SMe (and Me- $COCH_{2}SEt$, by analogy) as isolated, it follows that (I) = 0.648, (II) = 0.318 and (III) = 0.033. With these conformer populations, and the calculated dipole moments of I, II and III listed in Table 2, the dipole moments of Me-COCH₂SMe (and MeCOCH₂SEt) are calculated to be 2.24 D in carbon tetrachloride, and 2.15 D in benzene. First value compares well with the experimental moments of the compounds in carbon tetrachloride, 1.96 and 1.89 D respectively. Note that IR spectroscopy has indicated that MeCOCH₂SEt occurs as a mixture of *cis* and *gauche* conformers with (C)/(G) = 0.09 in carbon tetrachloride, 0.07 in n-hexane, and 0.23 in chloroform [2]. The discrepancy between the IR (C)/(G) value (0.09) and that drawn from molecular-mechanics energies ((III)/[(I)+II)] = 0.03 only) may be due to Onsager's reaction field which for a solute, as a rule, tends to increase the populations of the more polar conformers ($\mu(II) = 3.28 \text{ D}, \mu(III) = 3.94 \text{ D}$) relative to that of the other $(\mu(I) = 1.28 \text{ D})$ (see ref. 35).

^{*}A contact occurs when the C(2)-C(3)-S-p(S) is syn-periplenar (or nearly so), and a vicinity (neighbouring) when this chain is distorted by $\psi \sim 60^{\circ}$.



Fig. 3. More stable conformer (I or I') for $RCOCH_2SMe$ and $RCOCH_2SO_2Me$ (diagrammatic); X designates a sulphur lone-pair or an oxygen atom, R = Me or Ph.

Gauche conformer I virtually fulfils propitious criteria (a), (b) and (c) (Fig. 3); gauche conformer II displays a repulsive vicinity between one of the sulphur lone-pairs and the carbonyl-oxygen atom, and cis-like conformer III a repulsive $p(S)\cdots O$ vicinity and Me \cdots Me neighbouring (Fig. 2). In addition, unlike II and III, conforms I allows a large overlap between the σ_{C-S} and π_{C-O} orbitals causing some additional stabilization of this conformer (see refs. 1–3).

Onsager's reaction field in benzene solution, unlike that in carbon tetrachloride medium, cannot explain why (as suggested by the higher dipole moments of MeCOCH₂SMe and MeCOCH₂SEt in benzene, 2.13 and 2.14 D, as against 1.96 and 1.89 D in carbon tetrachloride), the relative populations of the more polar conformers II and III should be greater in benzene, because the dielectric permittivities of benzene and carbon tetrachloride are too close to each other (2.264 and 2.221) (cf. ref. 35). As for iodoacetone [5], this may be understood as follows: (i) aliphatic ketones (acetone, butan-2-one and pentan-2-one) give a complex with benzene, in which the adduct is located below the methyl and methyl(ene) groups [36]; (ii) this may occur for conformers II and III, but less (or not at all) for conformer I because here both sulphur lone-pair orbitals tend to repel the adduct. As a consequence, only II and III should be stabilized through complexation with benzene, making it so that the dipole moments of the compounds are somewhat increased on passing from carbon tetrachloride to benzene medium.

(2) The dipole moment of MeCOCH₂SO₂Me in benzene (3.19 D) is consistent with a mixture of gauche conformers I' and II', with (I')=0.78 and (II')=0.22. Calculated molecular-mechanics energy values for the compound in isolation suggest (I')=0.89 and (II')=0.11. The medium effect (in benzene) can explain the actual solution values of (II') and (I'), since $\mu(II')=4.76$ D as against $\mu(I')=2.56$ D.

Gauche conformer I' nearly fulfils all criteria (a), (b) and (c) (Fig. 3), while gauche conformer II' displays a repulsive $O(=S)\cdots O(=C)$ neighbouring (and the Me(-S) group in the HCH valley).

Preferred conformations of ω -methylthio- and ω -methylsulphonylacetophenone

In addition to the criteria of stability for MeCOCH₂SMe and Me-COCH₂SO₂Me conformers indicated above, it is necessary for the conformers of PhCOCH₂SMe and PhCOCH₂SO₂Me to take into account the Ph-CO conjugation energy which probably varies as $E = E_0 \cos^2 \tau$ [37], where τ is the Ph-CO rotational angle and E_0 may be taken as E(PhCOMe) = 7.1 kcal mol⁻¹ [38]. This effect only occurs for conformer IV' of PhCOCH₂SO₂Me having an Me····Ph neighbouring.

(1) Concerning PhCOCH₂SMe in isolation, molecular-mechanics energy values of conformers suggest a mixture of *gauche* conformer I and *cis*-shaped conformers II and III, with (I) = 0.982, (II) = 0.010 and (III) = 0.008 only. Clearly, the calculated dipole moments for such a mixture of conformers are lower than the experimental values of the compound in both carbon tetrachloride and n-hexane media, those being 1.69 and 1.76 D as compared to the observed values of 2.24 and 2.25 D respectively. This may be due to some uncertainty in the rather large differences E(II) - E(I) and E(III) - E(I) and, possibly, to the medium effect which tends to increase the relative populations of more polar II and III with respect to that of I.

Taking (II)/(III) as 1.35, from the mechanics energy values of II and III, the experimental dipole moments of PhCOCH₂SMe in carbon tetrachloride and n-hexane are consistent with the following mixtures: (I) = 0.84, (II) = 0.09 and (III) = 0.07; (I) = 0.85, (II) = 0.09 and (III) = 0.06. According to the present work, IR spectroscopy affords (C)/(G) = 0.08 in carbon tetrachloride, 0.09 in n-hexane and 0.17 in chloroform. First values are about twice as small as those ([(II) + (III)]/(I) = 0.19 and 0.18) estimated from the observed moments in carbon tetrachloride and n-hexane, respectively.

Gauche conformer I is similar to the more stable gauche conformer of MeCOCH₂SMe (Fig. 3), whilst *cis* conformer II exhibits one repulsive $p(S)\cdots O(=C)$ neighbouring and *cis* conformer III two $p(S)\cdots O(=C)$ vicinities.

(2) From the molecular-mechanics energy value of conformers, Ph-COCH₂SO₂Me as isolated appears as a mixture of gauche I', II' and IV' and cis-shaped III' and V', characterized by (I')=0.922, (II')=0.046, (III')=0.028, (IV')=0.003 and (V')=0.0013, whose dipole moment in benzene is calculated to be 2.83 D only as compared to the experimental value of 3.76 D. Such a high difference may be due to the solvent effect which tends to increase the relative populations of more polar II' and III' (and IV' and V') relative to much less polar I' (see Table 2).

Assuming that only I', II' and III' significantly contribute to the natural mixture of $PhCOCH_2SO_2Me$ in benzene solution, and that (II') = $1.64 \times (III')$ (from the actual energy values), the dipole moment of the compound in ben-

zene indicates a mixture of I', II' and III', with (I')=0.69, (II')=0.19 and (III')=0.12.

Gauche conformer I' virtually fulfils all criteria (a), (b) and (c) (Fig. 3); gauche conformer II' displays a repulsive $O(=S)\cdots O(=C)$ neighbouring; the cis conformer exhibits an $O(=S)\cdots O(=C)$ vicinity more repulsive than that in II' (because the actual $O\cdots O$ distance is smaller); gauche IV' displays a repulsive Me \cdots Ph neighbouring which can effect a large rotation of the phenyl group about the C_{ar} bond axis, and cis V' exhibits two repulsive $O(=S)\cdots O(=C)$ neighbourings.

CONCLUSIONS

From molecular-mechanics energy values, MeCOCH₂SMe (and Me-COCH₂SEt, by analogy), PhCOCH₂SMe and PhCOCH₂SO₂Me, as isolated, exist as definite mixtures of *cis*-like and *gauche* conformers, with the latter being predominant, whilst MeCOCH₂SO₂Me only occurs as two *gauche* conformers; among the *gauche* conformers, the one with the Me–S bond situated far away from the Me(-C) (or Ph(-C)) group, and nearly bisecting one of the C(=O)-C-H valleys, prevails in all cases (Fig. 3). The same situation holds for MeCOCH₂SO₂Me and PhCOCH₂SO₂Me in benzene, PhCOCH₂SMe in both carbon tetrachloride and n-hexane, as indicated by the electric dipole moments of the compounds in the specified medium.In the more stable *gauche* conformation of MeCOCH₂SMe (and MeCOCH₂SEt) and PhCOCH₂SMe, hyperconjugation of Me–S with the carbonyl bond can occur.

The fact that the more stable conformer is nearly the same for Me-COCH₂SO₂Me and MeCOCH₂SMe, PhCOCH₂SO₂Me and PhCOCH₂SMe, shows that the sulphonyl-oxygen atoms and sulphur lone-pairs play a similar role as the conformation-determining factor in these compounds.

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