Folded Conformations. Part 10.[1] Crystal and Molecular Structure of *p*-Dimethylaminophenyl *N*-Methyl-*N*-(*p*-nitrophenylsulphonylmethyl)-carbamate. Non-bonded Energy Calculations on Molecular Conformations

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The crystal and molecular structure at −160 °C of the title compound (2) has been determined from diffractometer data by direct methods. The structure of (2) was refined to *R* 0.095 for 3 462 independent reflections. The molecule resides in a folded conformation in which the carbonyl oxygen lies above the *p*-nitrophenyl ring. Non-bonded energy calculations reveal that a folded conformation is energetically favourable for one separated molecule. A similar conformation has previously been proposed on the basis of n.m.r. isotropic solution spectra. The intramolecular charge-transfer band in the visible spectrum of (2) cannot be explained in terms of ' through-space ' overlap between the donor and acceptor aromatic rings.

In previous studies [2-4] it was established that alkyl (1) and aryl *N*-methyl-*N*-(arylsulphonylmethyl)carbamates

$ArSO_2{\cdot}CH_2{\cdot}NMe{\cdot}CO_2X$

(1) $Ar = p\text{-}MeC_6H_4,\ X = Et$

(2) $Ar = p\text{-}NO_2{\cdot}C_6H_4,\ X = p\text{-}NMe_2{\cdot}C_6H_4$

(2) in solution favour folded conformations in which the ester alkyl or aryl moiety is positioned above the plane of the aromatic ring attached to the sulphonyl group. The major evidence was based on (i) intramolecular shielding effects in n.m.r. spectra [2,3] and (ii) the long-wavelength absorption maximum in the u.v. spectrum of (2) (at 440 nm, ε 30 l mol^{-1} cm^{-1}), which obeys Beer's law and is therefore attributable to an intramolecular charge-transfer interaction between the aromatic π-systems.[2] The crystal and molecular structure of (1), found by single-crystal *X*-ray diffraction methods,[5]

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[1] Part 9, I. J. Tickle, J. Hess, A. Vos, and J. B. F. N. Engberts, *J.C.S. Perkin II*, 1978, 460; Part 8; I. P. Bleeker and J. B. F. N. Engberts, *Rec. Trav. chim.*, 1977, **96**, 58.

[2] R. van Est-Stammer and J. B. F. N. Engberts, *Rec. Trav. chim.*, 1972, **91**, 1298.

[3] S. van der Werf and J. B. F. N. Engberts, *Rec. Trav. chim.*, 1970, **89**, 423.

[4] R. van Est-Stammer, Dissertation, University of Groningen, 1973.

[5] I. J. Tickle and J. B. F. N. Engberts, *J.C.S. Perkin II*, 1973, 2031.

supported the conformational preferences in solution.

It was inferred that an explanation for these observations is to be found (i) in the minimized intramolecular dipole interactions involving the polarized S–O bonds [2] and (ii) in the favoured position of the aryl ring with the 2*p* orbital of the sulphur-bonded carbon staggered between the sulphonyl oxygen atoms.[3] Recent work on urea derivatives (3) and (4) [6,7] which reside in folded conformations, however, revealed that a folding tendency could as well be a result of intramolecular van der Waals and repulsive interactions.

$[p\text{-MeC}_6H_4\cdot SO_2\cdot CH(Ph)\cdot NH]_2C{:}O$

(3)

$[p\text{-MeC}_6H_4\cdot SO_2\cdot CH_2\cdot NH]_2C{:}O$

(4)

In view of these results, an *X*-ray crystallographic investigation of (2) seemed worthwhile. Since the crystals are red, knowledge of the molecular geometry would also yield more information on the interactions which are responsible for the donor–acceptor interaction band.

EXPERIMENTAL

The compound was prepared as described in ref. 8 and suitable crystals were obtained by slowly cooling a saturated methanol solution. Initial cell-dimensions were determined from zero-layer Weissenberg photographs. A crystal with dimensions *ca.* 0.3 × 0.3 × 0.4 mm was mounted on a three-circle Nonius diffractometer, and cooled by a stream of cold nitrogen gas, produced by the cooling system described in ref. 9. Zirconium-filtered molybdenum radiation was used. For 52 observed reflections the angles θ, ϕ, and χ were optimized, and accurate cell-dimensions were calculated by a least-squares program from the $\sin^2\theta/\lambda^2$ values.

Crystal Data (*at* −160 °C).—$C_{17}H_{19}N_3O_6S$, $M = 393.4$. Monoclinic prismatic, $a = 19.778$ (17), $b = 13.507$ (7), $c = 6.900$ (3) Å, $\beta = 99.44(4)°$. $U = 1\,818.3$ Å^3, $D_m = 1.38$ (20 °C), $Z = 4$, $D_c = 1.43$ g cm^{-1}. Space group $P2_1/c$, Mo-K_α radiation, $\lambda = 0.710\,69$ Å; $\mu(\text{Mo-}K_{\bar\alpha}) = 2.23$ cm^{-1}.

The apparatus and crystal described above were used and the intensities of all independent reflections with $\theta \leqslant 30°$ were collected by the θ—2θ integrating scan technique. The intensities of the strongest reflections were reduced by attenuation filters in order to keep the counting rate within the linear range of the scintillation equipment. Every 50 reflections two reference reflections were measured, so that corrections for intensity variations in the primary beam and for possible deterioration of the specimen could be made. Especially towards the end of the measurement there appeared to be a systematic intensity decrease of up to 6%, whereas during the whole measurement random fluctuations of *ca.* 2% in the reference reflections were noticed. Owing to setting difficulties of the diffractometer, the intensities of the high-order region especially, could not be measured very accurately, since in this region neighbouring reflections easily enter the same scanning range, because of the large values of *b* and *c* and the short wavelength of the radiation used.

All calculations were performed at the University Computer Centre with a CDC Cyber 74 16 computer. Where possible an updated version of the '*X*-Ray' system of crystallographic programs [10] was used.

TABLE 1

Fractional atomic co-ordinates (× 10^4), with standard deviations in parentheses

	x/*a*	*y*/*b*	*z*/*c*
S(01)	4 164(1)	925(1)	431(1)
O(01)	844(2)	1 653(3)	75(6)
O(02)	1 181(2)	3 117(3)	457(6)
O(03)	4 564(1)	1 789(2)	143(3)
O(04)	4 154(1)	89(2)	−872(3)
O(05)	3 261(1)	−1 088(2)	4 667(3)
O(06)	3 384(1)	584(2)	4 887(3)
N(01)	1 289(2)	2 257(3)	290(4)
N(02)	4 108(2)	−360(2)	3 416(4)
N(03)	961(2)	−1 039(3)	8 358(4)
C(01)	2 004(2)	1 927(3)	354(5)
C(02)	2 519(2)	2 610(3)	761(5)
C(03)	3 195(2)	2 292(3)	828(4)
C(04)	3 307(2)	1 304(3)	412(5)
C(05)	2 780(2)	632(3)	−15(5)
C(06)	2 111(2)	944(3)	−34(5)
C(07)	4 462(2)	501(3)	2 897(5)
C(08)	4 294(2)	−1 347(3)	2 762(6)
C(09)	3 562(2)	−207(3)	4 366(5)
C(10)	2 676(2)	−1 044(3)	5 578(5)
C(11)	2 104(2)	−509(3)	4 792(5)
C(12)	1 528(2)	−525(3)	5 674(5)
C(13)	1 520(2)	−1 078(3)	7 411(5)
C(14)	2 100(2)	−1 649(3)	8 132(5)
C(15)	2 678(2)	−1 625(3)	7 240(5)
C(16)	909(2)	−1 756(3)	9 907(6)
C(17)	320(2)	−587(3)	3 784(6)
H(02)	2 407	3 375	1 029
H(03)	3 613	2 815	1 019
H(05)	2 921	−123	−280
H(06)	1 683	440	−329
H(071)	5 011	424	3 020
H(072)	4 398	1 139	3 792
H(081)	3 957	−1 545	1 423
H(082)	4 319	−1 889	3 923
H(083)	4 823	−1 274	2 573
H(11)	2 115	−26	3 550
H(12)	1 079	−114	5 029
H(14)	2 116	−2 122	9 400
H(15)	3 132	−2 025	7 890
H(161)	958	−2 478	9 272
H(162)	429	−1 682	10 449
H(163)	1 322	−1 632	11 113
H(171)	425	188	7 188
H(172)	−62	−747	8 294
H(173)	172	−999	6 040

Corrections for Lorentz and polarization effects were applied. No correction for absorption was made because of the small value of the absorption coefficient. After rejection of reflections with net negative intensity, 3 856 from the measured set of 5 392 reflections remained for the structure determination. For the contributing reflections the weight was obtained as $w_c = [\sigma_c(F)]^{-2}$, where $\sigma_c(F)$ is the standard deviation in $|F|$ due to counting statistics and errors in the filter factors.

The structure was determined by direct methods. After

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[6] R. M. Tel and J. B. F. N. Engberts, *J.C.S. Perkin II*, 1976, 483.

[7] R. J. J. Visser, A. Vos, R. M. Tel, and J. B. F. N. Engberts, *Rec. Trav. chim.*, in the press.

[8] R. van Est-Stammer and J. B. F. N. Engberts, *Rec. Trav. chim.*, 1971, **90**, 1307.

[9] F. van Bolhuis, *J. Appl. Cryst.*, 1971, **4**, 263.

[10] J. M. Stewart, G. J. Kruger, H. L. Ammon, G. Dickinson, and S. R. Hall, '*X*-Ray' System of Crystallographic Programs, University of Maryland Technical Report, TR 192, 1972.

calculation of the normalized structure factors, E, the program MULTAN [10] was run with 396 reflections with $E > 1.8$. From 16 sets of signs an E map was calculated for the set having the highest figures-of-merit. The maxima corresponding with nearly all non-hydrogen atoms were located. The missing ' heavy ' atoms were found by means of a difference-Fourier synthesis. Refinement was done with a least-squares program working with a full normal matrix.[10] Scattering factors for non-hydrogen atoms were taken from ref. 11, and from ref. 12 for hydrogen. Assuming isotropic thermal motion, we refined the parameters of the ' heavy ' atoms to R 0.147. At this stage of the refinement 394 reflections with $|F| < 3\sigma_c(F)$ were rejected. From a comparison of the $|F_o|$ and $|F_c|$ values of strong low-order reflections systematic errors due to extinction appeared to be negligible. The hydrogen atoms of the phenyl groups and of C(07) were put at geometrically reasonable positions. For the methyl groups the hydrogen-atom positions were located in a difference-Fourier synthesis. As a structure refinement tends to position the hydrogen atoms too close to the ' heavy ' atoms to which they are linked,[13] C–H bond lengths were constrained at 1.08 Å, while the H–C–H angles were kept constant. Further refinement was anisotropic for non-hydrogen atoms, while hydrogen atoms were refined isotropically. The weight was taken as $w = [w_c^{-1} + pK^2F_o^2]^{-1}$, where K is the F_o scale factor and $p = 0.000\,13$, chosen to minimize the variation of $\langle w(kF_o - F_c)^2\rangle$ with $|F_o|$. Final values for R and R' were 0.095 and 0.072, respectively, for the reflections used in the refinement. A difference map based on these reflections did not show maxima or minima with absolute values $>3\sigma$ or 0.6 eÅ^{-3}. The statistically significant guide to the goodness-of-fit of the parameters to the data, $G = \{[w\Delta^2(F)]/(N_o - N_v)\}^{\frac{1}{2}}$, was 1.29. Final atomic co-ordinates and their standard deviations are listed in Table 1. Observed and calculated structure factors and thermal parameters are listed in Supplementary Publication No. SUP 22209 (21 pp., 1 microfiche).*

DISCUSSION

Crystal Packing.—The packing of the molecules in the crystal is given in Figure 1; Figure 2 shows the molecular structure and the numbering of the atoms. Several short intermolecular contacts in the crystal are observed: (i) H(06) · · · N(03$^{\text{I}}$) 2.53 and H(06) · · · C(13$^{\text{I}}$) 2.56 Å, where superscript I denotes a molecule translated one cell dimension along the c axis; (ii) O(03) · · · H(083$^{\text{II}}$) 2.49, O(04) · · · H(071$^{\text{II}}$) 2.49, O(01) · · · H(162$^{\text{II}}$) 2.48, and O(01) · · · H(172$^{\text{II}}$) 2.39 Å, where superscript II refers to an inverted molecule; and (iii) O(06) · · · H(03$^{\text{III}}$) 2.32 Å, where superscript III denotes the molecule at $(x, -y + \frac{1}{2}, z + \frac{1}{2})$. Although all distances refer to hydrogen atoms fixed in calculated positions (C–H 1.08 Å), it seems reasonable to pick out especially these intermolecular contacts as being responsible for the hardness of the crystals.

Molecular Structure.—Table 2 lists bond lengths and interbond angles within the molecule. The molecule has a folded conformation, in which O(06) lies over C(04) 3.20 Å from the p-nitrophenyl plane. This makes the structure of compound (2) essentially different from that of compound (1) (see Figure 3), in which the ether oxygen was found above the p-tolyl plane.[5] The $ArSO_2\cdot CH_2\cdot NMe\cdot CO_2^-$ portion of the molecule has a comformation similar to that of (1) in that: (i) the carbamate moiety is practically planar, with distances from C(07) and C(08) to the plane through N(02), C(09), O(05), and O(06) of 0.07 and 0.04 Å; (ii) the amide bond N(02)–C(09) is rather long,[5] and (iii) the C(04) p_π orbital lies approximately in the plane through C(04)–S(01) and bisecting O(03)–S(01)–O(04). As can be seen from the relevant bond lengths and interbond angles, both aryl rings show significant deviations from D_{6h} symmetry. Dominicano and Vaciago [14-16] have studied the variation

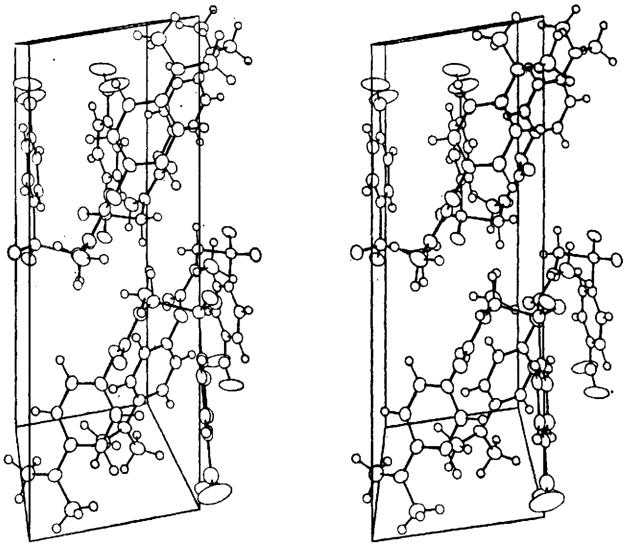

FIGURE 1 Stereoscopic view of the contents of the unit cell of (2) along the b axis

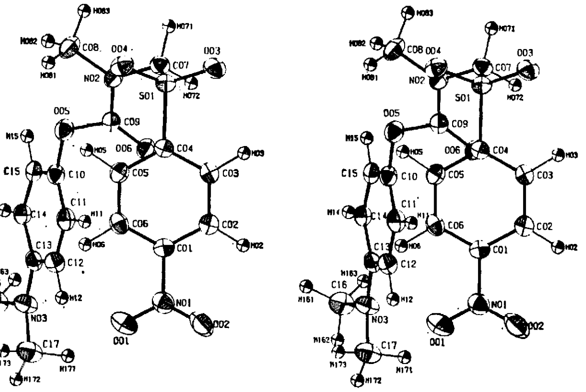

FIGURE 2 Stereoscopic view of the molecule of (2) showing the atom numbering scheme. Heavy atoms are shown at 50% probability. Hydrogen atoms were given a small arbitrarily chosen isotropic temperature factor

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* See Notice to Authors No. 7 in *J.C.S. Perkin II*, 1977, Index issue.

[11] D. T. Cromer and J. B. Mann, *Acta Cryst.*, 1968, **A24**, 321.

[12] R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.

[13] A. C. Larson, *Acta Cryst.*, 1967, **23**, 644.

[14] A. Dominicano, A. Vaciago, and C. A. Coulson, *Acta Cryst.*, 1975, **B31**, 221.

[15] A. Dominicano, A. Vaciago, and C. A. Coulson, *Acta Cryst.*, 1975, **B31**, 1630.

[16] A. Dominicano, P. Mazzeo, and A. Vaciago, *Tetrahedron Letters*, 1976, 1029.

of angle α at the *ipso* carbon atom with substituent X, and have provided possible explanations. Our angles α follow the same trend as do the literature values,[1,14-16] but are larger in all cases. This is possibly due to the fact that, whereas the structures referred to in the literature were determined at room temperature, ours was determined at −160 °C. In compounds of the type under investigation the aryl groups show relatively large librations around axes of the type C(01) · · · C(04), due to which atoms of the type C(02) are found to be too close to the libration axis making the observed values for the angles α too small. In our low-temperature case this decrease is relatively small so that for the angles α larger values are observed than for the room-temperature structures.

TABLE 2

Bond lengths (Å) and interbond angles (°) with standard deviations in parentheses

(*a*) Bond lengths			
N(01)–O(01)	1.192(5)	N(02)–C(08)	1.474(5)
N(01)–O(02)	1.189(5)	N(02)–C(09)	1.368(5)
N(01)–C(01)	1.478(5)	C(09)–O(06)	1.199(4)
C(01)–C(02)	1.369(5)	C(09)–O(05)	1.361(5)
C(02)–C(03)	1.396(5)	O(05)–C(10)	1.405(5)
C(03)–C(04)	1.390(5)	C(10)–C(11)	1.376(5)
C(04)–C(05)	1.379(5)	C(11)–C(12)	1.377(6)
C(05)–C(06)	1.385(5)	C(12)–C(13)	1.415(5)
C(06)–C(01)	1.377(5)	C(13)–C(14)	1.404(5)
C(04)–S(01)	1.769(4)	C(14)–C(15)	1.386(5)
S(01)–C(07)	1.801(4)	C(15)–C(10)	1.389(5)
S(01)–O(03)	1.441(3)	C(13)–N(03)	1.375(5)
S(01)–O(04)	1.442(3)	N(03)–C(16)	1.458(5)
C(07)–N(02)	1.433(5)	N(03)–C(17)	1.467(5)
(*b*) Interbond angles			
O(01)–N(01)–O(02)	122.7(3)	C(07)–N(02)–C(08)	120.0(3)
O(01)–N(01)–C(01)	118.7(3)	C(07)–N(02)–C(09)	117.0(3)
O(02)–N(01)–C(01)	118.5(3)	C(08)–N(02)–C(09)	122.7(3)
N(01)–C(01)–C(02)	118.7(3)	N(02)–C(09)–O(05)	110.0(3)
N(01)–C(01)–C(06)	117.6(3)	N(02)–C(09)–O(06)	124.8(3)
C(01)–C(02)–C(03)	118.4(3)	O(05)–C(09)–O(06)	125.2(3)
C(02)–C(03)–C(04)	118.2(3)	C(09)–O(05)–C(10)	116.4(3)
C(03)–C(04)–C(05)	122.4(3)	O(05)–C(10)–C(11)	122.0(3)
C(04)–C(05)–C(06)	119.3(3)	O(05)–C(10)–C(15)	117.0(3)
C(05)–C(06)–C(01)	118.0(3)	C(15)–C(10)–C(11)	120.9(4)
C(06)–C(01)–C(02)	123.8(3)	C(10)–C(11)–C(12)	120.2(3)
C(03)–C(04)–S(01)	117.5(3)	C(11)–C(12)–C(13)	120.6(3)
C(05)–C(04)–S(01)	120.1(3)	C(12)–C(13)–C(14)	117.9(3)
C(04)–S(01)–O(03)	108.2(2)	C(13)–C(14)–C(15)	121.1(3)
C(04)–S(01)–O(04)	107.8(2)	C(14)–C(15)–C(10)	119.3(3)
C(04)–S(01)–C(07)	105.3(2)	C(12)–C(13)–N(03)	120.3(3)
O(03)–S(01)–O(04)	120.1(2)	C(14)–C(13)–N(03)	121.8(3)
O(03)–S(01)–C(07)	106.6(2)	C(13)–N(03)–C(16)	118.8(3)
O(04)–S(01)–C(07)	108.0(2)	C(13)–N(03)–C(17)	120.0(3)
S(01)–C(07)–N(02)	113.4(2)	C(16)–N(03)–C(17)	116.9(3)

Charge Transfer.—The intramolecular charge-transfer band of (2) (at 440 nm, ε 30 l mol^{-1} cm^{-1}) has previously been attributed to spacial overlap between the π orbitals of the *p*-dimethylaminophenyl ring (donor group) and the *p*-nitrophenyl ring (acceptor group). Since the crystals are red, this overlap was expected to be maintained in the solid state. Interestingly, the present crystal structure determination shows that in the crystal neither intra- nor inter-molecular overlap of this above type occurs. Also, for the reddish crystals of $p\text{-NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{SO}_2\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{NMe}_2\text{-}p$ (5), for which a similar charge-transfer mechanism has been proposed [17] it was recently found that no spacial overlap was present between the donor and acceptor moieties.[1] Consequently, a different explanation is required for the charge transfer. In this connection it is noticeable that the angles θ(1) and θ(2) of compounds (2) (see Table 3) and (5) * are close to 90°. Therefore, through-bond interaction,[18] as suggested for instance for *N*-(*p*-methoxyphenylalkyl)pyridinium ions [19] and 1-aza-adamantane derivatives,[20] may well be possible.

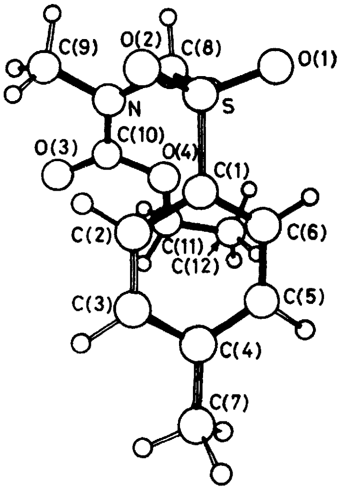

FIGURE 3 Structure of carbamate (1) and the atom numbering scheme

TABLE 3

Comparison of torsion angles (°) at which potential energy is minimal, with observed values for crystals; σ in observed values 0.3°

Angle	Calc.	Obs.
(*a*) Compound (2) *		
θ(1):† [C(01)—(06)]–C(04)–S(01)–C(07)	82.4, 265.7	92.1
ϕ: C(04)–S(01)–C(07)–N(02)	48.6	64.9
θ(2): S(01)–C(07)–N(02)–[N(02), C(09), O(05), O(06)]	86.6, 267.7	83.6
θ(3): [N(02), C(09), O(05), O(06)]–[C(10)–C(15)]	88.4, 273.9	57.1
(*b*) Compound (1) ‡		
θ(1): [C(1)—(6)]–C(1)–S–C(8)	89.6, 269.8	92.4
ϕ: C(1)–S–C(8)–N	60.8	56.3
θ(2): S–C(8)–N–[N, C(10), O(3), O(4)]	85.4, 270.4	82.7
θ(3): [N, C(10), O(3), O(4)]O(4)–C(11)–C(12)	−3.1	7.7

* For numbering see Figure 2. † Torsion angles ABCD are defined as 180° — dihedral angles between planes ABC and BCD, a positive angle means that in a Newton projection along BC the front atom has to be rotated clockwise to make the planes ABC and BCD coincide. In cases where A (or D) is replaced by atoms listed in square brackets, ABC (or BCD) is replaced by the best plane through these atoms. ‡ For numbering see Figure 3.

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* For compound (5) θ(1) and θ(2) are the torsion angles around C(aromatic)–S and around C(aliphatic)–C(aromatic).

[17] R. van Est-Stammer and J. B. F. N. Engberts, *Tetrahedron Letters*, 1971, 3215.

[18] R. Hoffmann, *Accounts Chem. Res.*, 1971, **4**, 1.

[19] A. J. de Gee, J. W. Verhoeven, W. J. Sep, and T. J. de Boer, *J.C.S. Perkin II*, 1975, 579.

[20] C. Worrell, J. W. Verhoeven, and W. N. Speckamp, *Tetrahedron*, 1974, **30**, 3525.

Intramolecular Non-bonded Interactions.—In order to investigate whether individual molecules (in vacuum) of compounds (1) and (2) would prefer conformations to those observed in the crystals, potential-energy calculations have been carried out by use of Busing's program WMIN.[21] Rotations around specific bonds were performed in order to find the conformations with minimal energy. Apart from these rotations, the molecules were considered rigid with geometries as found from the crystal structure determinations. In the calculations only attractive (van der Waals) and repulsive interactions were considered. Coulombic interactions were omitted since recent calculations on urea derivatives (3) and (4) showed that introduction of Coulombic forces hardly influences the positions of the minima in the potential-energy curves.[6,7] Thus, the potential energy was obtained on the basis of the Buckingham-type potential function [equation (1)] in which R_{ij} is the distance between the atoms i and j. The constants A_i, B_i, and C_i

$$E_{\text{nb}} = (A_i + A_j) \exp [(B_i + B_j - R_{ij})/(A_i + A_j)] - C_iC_j/R_{ij}^6 \quad (1)$$

were calculated from literature data for (homonuclear) potential-energy functions of the form of equation (2) by equating analogous parts of equations (1) and (2).

$$E_{\text{nb}} = A_{ij} \exp - B_{ij}R_{ij} - C_{ij}/R_{ij}^6 \quad (2)$$

The values of the constants A, B, and C were taken from ref. 22 for carbon and hydrogen, from ref. 23 for sulphur, from ref. 24 for oxygen, and from ref. 25 for nitrogen.

In compound (2) we performed rotations around C(04)–S(01), S(01)–C(07), C(07)–N(02), and O(05)–C(10), while the remaining portions of the molecule were kept rigid. The following calculations were carried out.

(*a*) Successive rotations around the bonds, each time starting from the crystal conformation. In Table 3 dihedral angles at which energy minima are found are compared with the observed values for the crystal. The minimum for rotation around C(07)–N(02) given in Table 3 is very steep owing to the fact that even a small rotation makes the distances O(06) ··· C(04) or C(08) ··· O(04) too short (the minimum at θ(1′) = θ(1) + 178.9° is analogous). In Figure 4 the energy changes on variation of ϕ [*i.e.* rotation around S(01)–C(07)], which represents folding and unfolding of the molecule, are plotted as a function of ϕ.

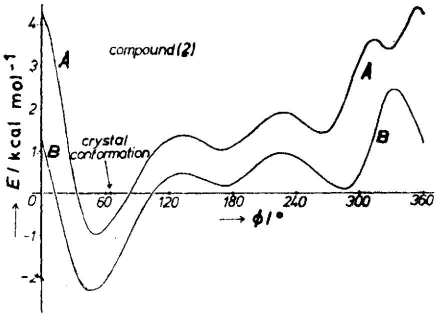

FIGURE 4 Variation of the calculated potential energy E as a function of ϕ for carbamate (2). For methods of calculation see text: A calculated by equation (1), B by equation (2)

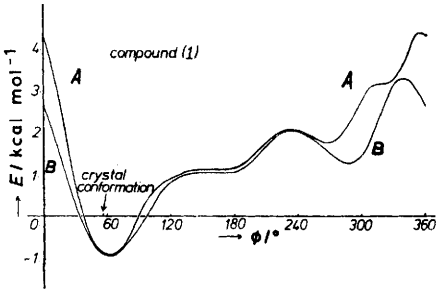

FIGURE 5 Variation of the calculated potential-energy E as a function of ϕ for carbamate (1); A and B calculated as for Figure 4

(*b*) Rotation around S(01)–C(07) with simultaneous energy minimization by rotation around C(04)–S(01) and O(05)–C(10). The curve giving the minimal values of the energy as a function of ϕ is given in Figure 4.

Similar calculations were carried out for carbamate (1). The results are shown in Table 3 (see also Figure 3) and in Figure 5. Apart from θ(3) the results are strongly analogous to those obtained for (2). For (1), rotation around O(04)–C(11) shows only one minimum due to the fact that the ethoxy-group does not show pseudo-two-fold symmetry about this bond.

Table 3 shows that, apart from the dihedral angle θ(3) of compound (2), the differences between the calculated dihedral angles and those observed in the crystal are smaller than 17°. The large calculated value for θ(3) of compound (2) may be a result of the neglect of resonance energy between the carbamate moiety and the *p*-dimethylaminophenyl group in the potential-energy function. In all cases the energy difference between the observed and calculated conformations is small: 1.0 kcal mol^{-1} for θ(3) in compound (2) and <0.3 kcal mol^{-1} for the other rotations. The calculated preferred conformations are generally not affected too strongly by intermolecular interactions in the crystals. Since similar conformations have been suggested in solution and in the solid state,[2-4] it may be inferred that in solution the influence of intermolecular interactions (solvent effects) on the molecular conformations will also be small. From the results depicted in Figures 4 and 5 we conclude that the energy differences on unfolding of the molecules are presumably small enough to allow the molecule to reside in conformations different from the favoured folded one. The same conclusion has been reached previously in a study of intramolecular shielding effects in the n.m.r. spectra of the *E*- and *Z*-conformations (due

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to hindered rotation around the N–CO bond) of aryl *N*-(arylsulphonylmethyl)-*N*-methylcarbamates.[2]

Finally we note that the agreement obtained between calculated and observed conformations indicates that potential-energy functions of the Buckingham type are a reasonable model for this kind of calculation, and that most likely the effect of dipole interactions involving the sulphonyl group [2] has previously been overestimated.

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