

DIPOLE MOMENTS AND CONFORMATION OF ALKYL ISOTHIOCYANATOCARBOXYLATES*

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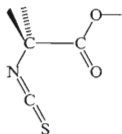
The solution dipole moments of alkyl isothiocyanatocarboxylates *I–VI, VII*, and *VIII* — containing one, three, and five carbon atoms, respectively, between the functional groups — are close to the values computed for the free rotation around all the bonds involved. With most 2-isothiocyanatocarboxylates the conformations near to *sc-sp* (*B*) seem to be slightly more populated due to the electrostatic attraction between the carbonyl oxygen and the carbon atom of the NCS group. This interpretation agrees even with the small differences found between the dipole moments of individual compounds. Hence the conclusions obtained previously from the IR spectroscopy have been confirmed, though only qualitatively.

In our previous communications we dealt with an improved synthesis¹, physical properties^{1,2}, and reactivity³ of the title compounds. With 2-isothiocyanatocarboxylates the problem of the conformation on the two adjoining bonds, C—N and C—C, deserves attention. We interpreted the doubled carbonyl band in the IR spectrum by the presence of two conformers and assumed that the more abundant of them is stabilized by the electrostatic interaction between the carbonyl oxygen and the isothiocyanato group¹; its exact conformation might be either¹ *sp-sp* (*A*) or, more probably², *sc-sp* (*B*). This explanation was also consistent with the solvent shifts of the C=O band² as well as with the temperature dependence of ¹H-NMR spectra². All this evidence is, of course, only indirect; in particular the conformation of the second rotamer has remained virtually unknown and the population could be estimated only very roughly.

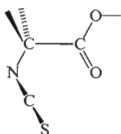
For these reasons we made use of the dipole moment approach whose results are reported in this paper. The compounds under study included six 2-isothiocyanatocarboxylates *I–VI* (Table I) with substituents of varying steric requirements

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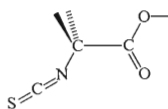
and two derivatives with a more distant NCS group (*VII*, *VIII*). The experimental dipole moments were compared with those computed for the various possible conformations, e.g. *A–F*, by the vector addition of bond moments⁴.



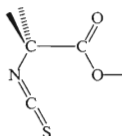
A (*sp-sp*)
 $\tau_1 = \tau_2 = 0^\circ$
 $\mu_{\text{calc}} = 4.88$



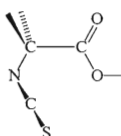
B (*sc-sp*)
 $\tau_1 = 60^\circ, \tau_2 = 0^\circ$
 $\mu_{\text{calc}} = 4.68$



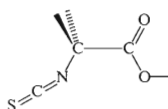
C (*ap-sp*)
 $\tau_1 = 180^\circ, \tau_2 = 0^\circ$
 $\mu_{\text{calc}} = 4.03$



D (*sp-ap*)
 $\tau_1 = 0^\circ, \tau_2 = 180^\circ$
 $\mu_{\text{calc}} = 2.14$



E (*sc-ap*)
 $\tau_1 = 60^\circ, \tau_2 = 180^\circ$
 $\mu_{\text{calc}} = 2.07$



F (*ap-ap*)
 $\tau_1 = \tau_2 = 180^\circ$
 $\mu_{\text{calc}} = 1.88$ *D*

EXPERIMENTAL AND RESULTS

Materials: The alkyl isothiocyanatocarboxylates *I–VIII* were described previously^{1,2}.

Physical measurements: Dielectric constants and densities of benzene solutions were determined at 25°C, usually at five concentrations within the range 0.005–0.05M. A heterodyne apparatus with frequency 1.2M Hz was used. The dipole moments were evaluated according to Halverstadt and Kumler⁵. The molar refractions of four compounds were determined experimentally and the average increment of 16.0 cm³ was derived for the —NCS group using Vogel's system of increments⁶, valid at 20°C. The molar refractions of the remaining compounds were calculated with this value. The correction for the atomic polarization of 5% or 15% of the R_D value was applied. All the results are listed in Table I.

Calculations: The dipole moments expected for the individual conformations were calculated using the standard values of bond moments⁴: H—C_α 0.3 D, C—O 0.74 D, C=O 2.5 D, C—N 0.45 D. The group moment of the —NCS group in aliphatic derivatives was estimated to 3.03 D at the angle of 29° to the C—N bond by the following reasoning. From the experimental dipole moments of methyl⁷, ethyl⁷, and 2-methyl-2-propyl⁸ isothiocyanates we chose the value of 3.3 D as typical for aliphatic, not very branched derivatives. Using the known geometry of methyl isothiocyanate⁹, we resolved this value into components, *viz.* the H—C and C—N bond moments

acting along the C—N bond and the rest acting in the N=C=S direction. The two latter components together represent the NCS group moment.

The bond angles used were $\angle \text{C—N—C} = 147^\circ$ (ref.⁹), $\angle \text{N—C—C} = \angle \text{C—C—C} = 111^\circ$, $\angle \text{C—C=O} = 116^\circ$, $\angle \text{O=C—O} = 124^\circ$, $\angle \text{C—O—C} = 113^\circ$. The dipole moments for the free rotation were calculated according to the known formula⁴; their values are listed in Table I, last column. The other calculated values are represented graphically in Fig. 1.

The estimation of the electrostatic interaction was based on the above bond angles, on the bond lengths measured on methyl isothiocyanate⁹ (C—N 1.45 Å, C=N 1.22 Å, C=S 1.56 Å), and on usual bond lengths for the rest of the molecule (C—C 1.52 Å, C=O 1.21 Å, OC—O 1.34 Å, O—C 1.44 Å). The results are not sensitive to these values. The charges on individual atoms were obtained by dividing each bond moment by the respective bond length and summing up at each atom. The group moment of the —NCS group was resolved in such a manner that components corresponding to common bond moments C—N, C=N (1.8 D), and C=S (2.95 D)

TABLE I
Dipole Moment Data of Alkyl Isothiocyanatocarboxylates I—VIII (Benzene, 25°C)

Compound	n_D^{20} d^{20}	α^a β^a	P_D^0, cm^3 R_D^{20}, cm^3	$\mu(5)^b, \text{D}$ $\mu(15)^b, \text{D}$	μ_{calc}^c D
I SCNCH ₂ COOCH ₃	1.5182	11.12	305.3	3.64	3.47
	1.2255	-0.340	32.44	3.62	
II SCNCH ₂ COOC ₂ H ₅	1.5080	10.22	315.5	3.68	3.47
	1.1671	-0.294	37.08	3.66	
III SCNCH ₂ COOCH(CH ₃) ₂	1.4938	10.47	356.2	3.91	3.47
	1.1064	-0.236	41.88	3.88	
IV (±)-SCNCH(CH ₃)COOC ₂ H ₅	—	8.14	286.3	3.44	3.47
	—	-0.240	41.8 ^d	3.41	
V (±)-SCNCH(C ₂ H ₅)COOC ₂ H ₅	—	8.01	308.7	3.56	3.47
	—	-0.213	46.5 ^d	3.53	
VI SCNC(CH ₃) ₂ COOC ₂ H ₅	1.4807	6.72	267.8	3.26	3.47
	1.0540	-0.194	46.75	3.23	
VII SCN(CH ₂) ₃ COOC ₂ H ₅	—	7.92	303.6	3.52	3.66
	—	-0.256	46.5 ^d	3.49	
VIII SCN(CH ₂) ₅ COOC ₂ H ₅	—	8.27	370.2	3.90	3.68
	—	-0.185	55.8 ^d	3.87	

^a Slopes of the Halverstadt-Kumler plots⁵, ϵ vs w_2 and d^{-1} vs w_2 , respectively; ^b correction for the atomic polarization 5% or 15% of the R_D value, respectively; ^c calculated for the free rotation around all the C—C and C—N bonds; ^d calculated from increments using the value of 16.0 cm³ for the NCS group.

were vectorially subtracted, the rest — attributed to the contribution of the mesomerie formula $R-N^{(+)}\equiv C-S^{(-)}$ — was divided by the distance $N-S$ and the charges were added to these two atoms. The dielectric constant used was that of benzene (2.274).

DISCUSSION

To begin with, let us restrict the discussion to alkyl 2-isothiocyanatocarboxylates *I–VI*; their calculated dipole moments are identical within the framework of the bond moment scheme and even the experimental moments do not differ too much. In order to deduce the approximate conformation, the following points are pertinent:

1. The conformation is described by two dihedral angles, $\tau_1 = \angle C=N-C-C$ and $\tau_2 = \angle N-C-C=O$ which should be determined on the basis of one dipole moment value. Hence a unique solution cannot in principle be obtained.

2. There is no pronounced steric hindrance in any of the possible conformations, so that these may be controlled only by relatively weak electrostatic interactions. Hence the conformation analysis does not allow to exclude any conformation or to give one of them clear preference; the presence of several forms in appreciable amounts is to be expected. (Compare the mentioned arguments^{1,2} from the IR and NMR spectroscopies.)

3. Even the two barriers to internal rotation are certainly very low, see *e.g.* the barriers in methyl isothiocyanate⁹ (350 cal mol⁻¹) or in acetic acid and similar compounds¹⁰ with a $C_{sp^2}-C_{sp^3}$ bond. Hence each conformation considered will actually represent the mean of a set of related forms.

These general considerations are confirmed by the analysis of dipole moment data. The calculated dipole moments are plotted in Fig. 1 in the form of a contour

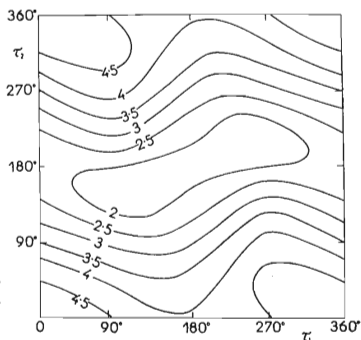


FIG. 1
Contour Map of Calculated Dipole Moments
(in D units) of Alkyl 2-Isothiocyanato-
carboxylates *I–VI* as a Function of Di-
hedral Angles τ_1 and τ_2

map. Evidently, the experimental values (3.2–3.9 D) could correspond to many pairs of the dihedral angles τ_1 , τ_2 , but of the conformations so defined none can be given preference. In this respect we agree fully with the opinion¹¹ that a definite conformation must not be assigned in this way, unless an energy minimum actually exists. On the other hand, just an opposite approximation is possible which assumes completely free rotation around the two bonds, C—N and C—C, *i.e.* equal population of all possible conformations. The calculated values (Table I) are rather close to the experimental ones. This means in reality that several forms within the range of τ 0–360° are present in comparable amounts; the term “free rotation” is to be understood only as a mathematical simplification⁴. As possible alternatives we considered even models with one moiety freely rotating and the other in a fixed position. If the —COOR group were fixed it would be in a rather improbable position with $\tau_2 \approx 90^\circ$; if —NCS were fixed, its position would influence the dipole moment very little and τ_1 could not be determined. We do not see, however, any reason why one barrier should be much higher than the other; and prefer the model with both barriers equally low.

A closer inspection reveals differences between compounds *I–VI*; in particular the derivatives of acetic acid, *I–III*, show higher dipole moments than calculated for the free rotation. A possible explanation is large population of the forms near to *A* (say, up to *B*) as we suggested previously^{1,2}. Since the factors preferring these conformations must be mostly of electrostatic nature, we attempted to calculate the electrostatic energy for the planar forms *A*, *C*, *D*, *F* in a simple manner described in Experimental. This approach^{12–14} was criticized¹⁵ in the case of adjoining groups but yielded some reasonable results if these groups are sufficiently distant^{13,14}. An additional uncertainty originates in our case from resolving the —NCS group moment, however, the calculated charges agree fairly well with the INDO calculations¹⁶ for the HNCS molecule. Hence we must be satisfied that the results are at least of reasonable order: The relative electrostatic energy of the forms *A*, *C*, *D*, *F* was calculated to 0, 770, 510, 260 cal mol⁻¹, respectively. If the mixture only of these four rotamers in the proper population were considered, its effective dipole moment would be 3.64 D. The coincidence with the experimental value of *I* is, of course, merely accidental but we may conclude that the interpretation in terms of the electrostatic interaction between functional groups is acceptable and that this interaction is attractive rather than repulsive in character. Some mutual influencing of the two groups is revealed even by the molar refraction, our increment of the NCS group (16.0 cm³) being significantly higher than that derived on alkyl isothiocyanates⁶ (15.6 cm³).

To summarize, the model preferred by us assumes low barriers of rotation and simultaneous presence of several rotamers; of these a group of forms between *A* and *B* is slightly favoured by electrostatic forces. Although the barrier is low, the

energy minimum lies rather nearer to *B* than to *A*. This concept is not contradictory to our previous results^{1,2}, we must only assume that several rotamers or a group of related rotamers may be responsible for one observed carbonyl band. If one carbonyl band was attributed^{1,2} solely to the rotamer *A* (of *B*), its population was probably overestimated as follows from the above calculations and from the dipole moment data. For instance, the dipole moment of *I* calculated for the population as given earlier¹ would be too high, *viz.* 4.10 D for the mixture of *A* and *D* forms, or 3.95 D for *B* and *E* forms.

On the basis of the same model we can now explain even the small differences between the dipole moments of compounds *I–VI*, referring to the steric demands of the alkyl groups involved. The increase in sequence *I, II, III* is attributed to the steric hindrance within the ester moiety, favouring the conformation *A* (*B*) against *D* (*E*). Even the α -substitution in the compounds *IV, V, VI* influences probably more the ester group – favouring the conformations *D, E* against *A, B* and lowering the dipole moment – than the isothiocyanate group since suppressing the forms *C* and *F* would slightly increase the dipole moment. The steric effects are significant in this case since they dominate the possible electrostatic induction which would increase the dipole moment, too (compare the moment of 2-methyl-2-propyl isothiocyanate⁸).

All the conclusions reached depend rather sensitively on the precision of the calculated values; hence it was desirable to check the calculations on some structurally different molecules. The possible variations of structure are, however, very restricted, in particular rigid model compounds do not exist. We can refer only to derivatives *VII* and *VIII* with three or five methylene groups, respectively, between the two functional groups. For such molecules the free rotation around all the bonds involved is usually a satisfactory approximation⁴. The dipole moment of *VII* is not enhanced like in *I–III* and agrees well with the assumed free rotation. Dreiding models show that even the conformations with near C=O and NCS groups allow different orientation of dipoles. The moment of *VIII* is again higher and preferred conformations cannot be estimated in this case.

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