The Conformation around Two Equivalent Bonds linked to One Central Atom: Diacyl Sulphides and Sulphonic Acid Anhydrides and Thioanhydrides

By **Otto Exner,*** Institute of Organic Chemistry and Biochemistry, Czechoslovak Academy of Sciences, 166 10 Prague, Czechoslovakia
Pasquale Dembech, Giancarlo Seconi, and **Piero Vivarelli,*** Laboratorio del C.N.R. dei composti del carbonio contenenti eteroatomi e loro applicazioni, Ozzano E., Bologna, and Istituto di Chimica Organica della Università, Modena, Italy

The conformations of the title compounds have been deduced from a dipole moment measurement in benzene solution. In all cases the C_2 form prevails, *i.e.* (A) and (C), with a dihedral angle τ of *ca.* 160 and 60°, respectively. Summarizing the available information, the conformation on two equivalent bonds linked to a central atom is the same as in the corresponding monofunctional derivatives, with slight distortion, if any. When, as in the case of nonplanar groups, there are two possibilities, the C_2 conformation is preferred to the C_s.

In previous papers[1] we examined the conformations around two equivalent single bonds attached to a common central atom. The main problems involved are the following. (i) The conformation around each bond may be analogous to that of the corresponding monofunctional derivative, or it may be distorted by steric repulsion in the more crowded molecule. This phenomenon is part of a broader problem, namely that of predicting the conformation of a complex molecule on the basis of simpler ones. (ii) Even when the conformation of simpler molecules is retained, several possibilities may arise in the case of nonplanar groups. The equivalence of the two bonds suggests a symmetrical arrangement around them, *i.e.* either C_2 or C_s symmetry of the whole group. These possibilities are controlled by subtle secondary factors.

In the present work we have extended our studies to diacyl sulphides (1)—(3), and to anhydrides (4)—(6), and thioanhydrides (7)—(9) of sulphonic acids (see Table 1). Their conformations are to be compared with those of simpler model molecules,[2] *viz. S*-alkyl thioesters,[2a] alkyl sulphonates,[2b] and *S*-alkyl thiosulphonates,[2c,3] respectively. In the series of compounds studied here, only the conformation of diacyl sulphides has already received attention.[4] We made use of the dipole moment approach,[1,2] combined with the graphical method of evaluation.[5] The main purpose of this paper is to summarize the results hitherto obtained and to draw some general conclusions.

RESULTS

The experimental results are listed in Table 1. The accuracy in the dipole moments is ±0·05 D in addition to

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[1] (*a*) O. Exner, V. Jehlička, and B. Uchytil, *Coll. Czech. Chem. Comm.*, 1968, **33**, 2862; (*b*) O. Exner and V. Jehlička, *ibid.*, 1970, **35**, 1514; (*c*) O. Exner, V. Jehlička, and J. Firl, *ibid.*, 1972, **37**, 466; (*d*) O. Exner and V. Jehlička, *ibid.*, p. 2169; (*e*) O. Exner, L. Almasi, and L. Paskucz, *ibid.*, 1973, **38**, 677.

[2] (*a*) O. Exner, V. Jehlička, and J. Firl, *Coll. Czech. Chem. Comm.*, 1971, **36**, 2936; (*b*) O. Exner, Z. Fidlerová, and V. Jehlička, *ibid.*, 1968, **33**, 2019; (*c*) O. Exner, D. N. Harpp, and J. G. Gleason, *Canad. J. Chem.*, 1972, **50**, 548.

[3] N. I. Grishko and E. N. Gurianova, *Zhur. fiz. Chim.*, 1958, **32**, 2725.

[4] (*a*) J. H. Markgraf, G. A. Lee, and J. F. Skinner, *J. Phys. Chem.*, 1968, **72**, 2276; (*b*) P. A. Hopkins and R. J. W. Le Fèvre, *J. Chem. Soc.* (*B*), 1971, 338.

[5] O. Exner and V. Jehlička, *Coll. Czech. Chem. Comm.*, 1965, **30**, 639.

the uncertainty arising from the correction for atomic polarization (represented by the difference between the two final columns in Table 1). Owing to the instability of compounds (4)—(6), the experimental values are somewhat less reliable. The dipole moments of compound (1) and (3) are very close to those of the corresponding carboxylic acid anhydrides.[1b]

Theoretical moments for various conformations were calculated by vector addition of the following bond moments: H–C$_{al}$ 0·3, H–C$_{ar}$ 0·0, C=O 2·5, C–S 0·9, C$_{ar}$–Cl 1·6, S–O 0·2, and SO$_2$ group moment 3·2 D. In addition, mesomeric moments of 0·25 for the conjugated PhCO and 1·0 D for the conjugated PhSO$_2$ functions, in the direction C$_{ar}$–C and C$_{ar}$–S, respectively, were employed. Only the C–S bond moment has been somewhat changed in the light of recent findings,[6] but this change from the bond moments hitherto used[2] is unimportant for the final results. The bond angles used were: $\mathrm{C{-}\hat{C}{=}O}$ 116, $\mathrm{O{=}\hat{C}{-}S}$ 124, $\mathrm{C{-}\hat{S}{-}C}$ 102, $\mathrm{C{-}\hat{S}{-}O}$ 102, $\mathrm{S{-}\hat{O}{-}S}$ 116, and $\mathrm{S{-}\hat{S}{-}S}$ 106° (see refs. 2, 4*b*, and 7).

TABLE 1

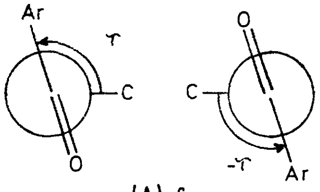
Polarization and dipole moments of diacyl sulphides (1)—(3) and sulphonic acid anhydrides (4)—(6) and thioanhydrides (7)—(9) in benzene at 25°

Compound	R_D^{20}/cm^3 [a]	$_\infty P_2$/cm^3	μ(5%)/D [b]	μ(15%)/D [b]
(1) $(C_6H_5CO)_2S$	69·5	353·6	3·70	3·65
(2) $(4\text{-}MeC_6H_4CO)_2S$	78·9	420	4·06	4·01
(3) $(4\text{-}ClC_6H_4CO)_2S$	79·4	238·7	2·76	2·69
(4) $(C_6H_5SO_2)_2O$	69·8	551	4·83	4·80
(5) $(4\text{-}MeC_6H_4SO_2)_2O$	79·2	669	5·35	5·30
(6) $(4\text{-}ClC_6H_4SO_2)_2O$	79·7	261·3	2·95	2·88
(7) $(C_6H_5SO_2)_2S$	76·0	320·8	3·42	3·37
(8) $(4\text{-}MeC_6H_4SO_2)_2S$	85·4	348·7	3·55	3·50
(9) $(4\text{-}ClC_6H_4SO_2)_2S$	85·8	257·1	2·86	2·78

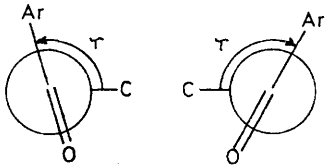
[a] Calculated from the atomic and group increments reported by A. I. Vogel, *J. Chem. Soc.*, 1948, 1833. Corrections for conjugation PhCO 0·7, CO–S–CO 0·3, PhSO$_2$ 0·4, and SO$_2$–O–SO$_2$ or SO$_2$–S–SO$_2$ 0·2 cm^3 have been made according to refs. 1*b* and 2*b*. [b] Correction for atomic polarization 5 or 15% of the R_D value, respectively.

Two kinds of conformation were considered in each case, according to the position of the two benzene rings with respect to the plane of the three central atoms X–Y–X, *viz.* C–S–C in compounds (1)—(3), S–O–S in compounds (4)—(6), and S–S–S in compounds (7)—(9). In the first conformation (C_2) the two aryl groups lie on different sides of this plane, and the dihedral angles $\tau = \mathrm{C_{ar}{-}X{-}\hat{Y}{-}X}$ have equal values and opposite signs,* as shown by the two Newman projections (A) for compounds (1)—(3), and (C) for compounds (4)—(9), viewed along the two X–Y bonds. In the second conformation (C_s) the angles τ have equal signs,* so that the two aryl groups are on the same side of the X–Y–X plane, as represented in the Newman projection (B) and (D).

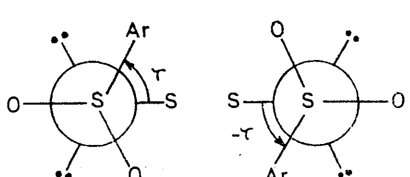
The computed moments are compared with the experimental ones in Figures 1—3. In the conjugated molecule of diacyl sulphides the planar forms, (E)—(G), are considered first; the doubly synperiplanar * form (G) would correspond exactly to the conformation of esters and thiolesters.[2a] From Figure 1 it appears that the diacyl sulphide



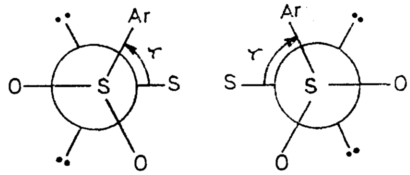
(A) C_2



(B) C_s



(C) C_2



(D) C_s

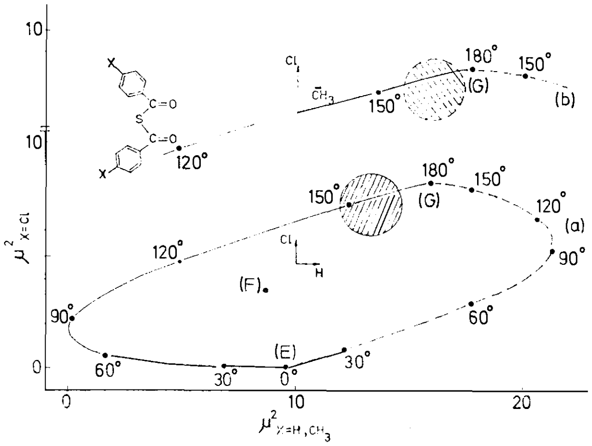


FIGURE 1 Comparison (a) of squared dipole moments $\mu^2_{X=H}$ *vs.* $\mu^2_{X=Cl}$ and (b) $\mu^2_{X=CH_3}$ *vs.* $\mu^2_{X=Cl}$ of compounds (1) and (3) and (2) and (3), respectively. Dots represent the moments calculated for conformations (A) (full curve) and (B) (broken curve); the dihedral angle τ is given. Hatched circles refer to the experimental dipole moments

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* In order to allow comparison of monofunctional and bifunctional derivatives, the signs of τ have been chosen as indicated in the Newman projections (A)—(D). The synperiplanar notation (*sp*) refers, according to the nomenclature rules, to the position of C=O and S–C bonds in (A) or (B), corresponding to τ = 180°.

[6] (*a*) A. N. Vereshchagin and O. Exner, *Coll. Czech. Chem. Comm.*, 1973, **38**, 690; (*b*) C. W. N. Cumper, *Tetrahedron*, 1969, **25**, 3131.

[7] (*a*) A. J. de Kok and C. Romers, *Rec. Trav. chim.*, 1969, **88**, 625; (*b*) A. M. Mathieson and J. M. Robertson, *J. Chem. Soc.*, 1949, 724.

molecule is actually slightly distorted, so that it may be represented by the Newman projection (A) with τ = 140—170°. Essentially the same C_2 conformations were found for diacetyl sulphide (τ = 133°) and acetic anhydride (τ = 135°) from the Kerr constant,[4b] for aromatic acid anhydrides (τ = 150—180°) from dipole moments,[1b] and for chloroacetic anhydride in the crystalline state [7a] (τ = 151 or 163°). In a dipole moment study of diacetyl sulphide different results were claimed,[4a] but they are impaired by the *a priori* assumption that only strictly planar forms are possible. It follows that the stable *sp* conformation of thioesters [2a] and esters [2b] is repeated twice in the conformation of diacyl sulphides and acid anhydrides, respectively, with a slight distortion due to steric and/or electrostatic repulsion of the two carbonyl oxygens in the strictly planar form (G).

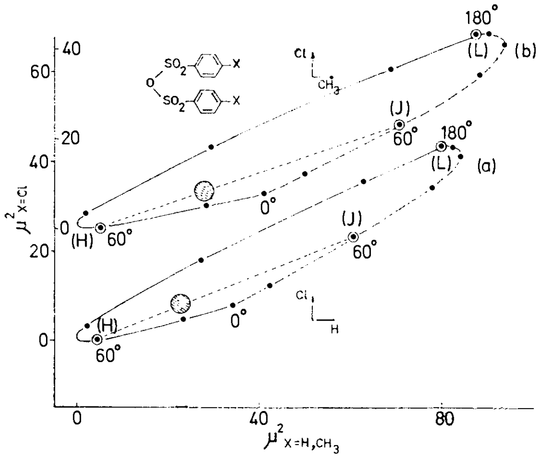


FIGURE 2 Comparison (a) of squared dipole moments $\mu^2_{X=H}$ *vs.* $\mu^2_{X=Cl}$ and (b) $\mu^2_{X=CH_3}$ *vs.* $\mu^2_{X=Cl}$ of sulphonic acid anhydrides (4) and (6) and (5) and (6), respectively. Dots refer to the moments calculated for conformations (C) (full curve) and (D) (broken curve). Staggered conformations (H), (J), and (L) are represented by empty points. Hatched circles refer to the experimental dipole moments

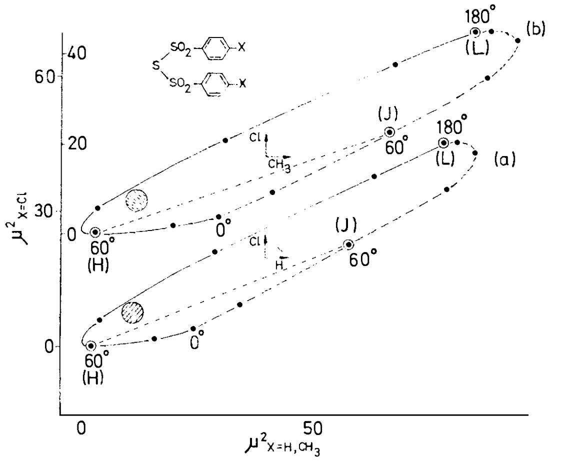
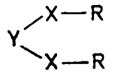
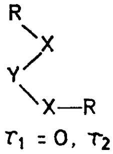


FIGURE 3 Comparison (a) of squared dipole moments of sulphonic acid thioanhydrides (7) and (9) and (b) (8) and (9). Empty points represent conformations (H), (J), and (L) (see Figure 2 for details)



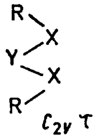
C_{2v} $\tau_{1,2}$ = 0°

(E)



C_s τ_1 = 0, τ_2 = 180°

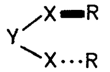
(F)



C_{2v} $\tau_{1,2}$ = 180°

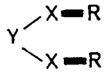
(G)

In view of the conformation of sulphonic [2b] and thiosulphonic [2c] esters, that of sulphonic anhydrides and thioanhydrides may be expected to be *gauche* (τ = 60°), but two possibilities still remain, *viz.* (H) and (J), corresponding to the Newman projections (C) and (D), respectively. Figures 2 and 3 reveal that the C_2 form (H) clearly predominates, probably accompanied by some (J) form (20 and 33% for thioanhydride and anhydride, respectively, estimated from the distances between the calculated and experimental points [5]). Similar results were obtained for structurally similar *gem*-disulphones in solution,[1c] while the conformation of compound (7) is completely of the C_2 form (H) in the crystalline state.[7b] In all cases, the conformation seems to be controlled by the *gauche*-interaction [8] of the two polar bonds C–SO$_2$ and O–C (S–C).



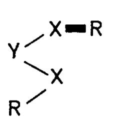
C_2 τ_1 = 60, τ_2 = 300°

(H)



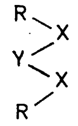
C_s $\tau_{1,2}$ = 60°

(J)



C_1 τ_1 = 60, τ_2 = 180°

(K)



C_{2v} $\tau_{1,2}$ = 180°

(L)

DISCUSSION

In order to discuss the problem of the conformation around two equivalent bonds in general, let us consider a functional group C–X–Y–X–C where the atoms X and Y may bear still further substituents. Two main cases may be distinguished. (1) When the conformation of X is planar and X is conjugated with Y, then the simple model molecule R–X–Y–R is also planar as a rule (insofar as there are no strong steric interactions). In this case the planar arrangement most probably applies to the whole molecule R–X–Y–X–R, too. Moreover, the three possibilities (E)—(G) must also be considered. Table 2 summarizes the available data obtained in solution by the dipole moment approach. In all monofunctional model compounds the angle τ is 180°, and this is largely preserved in bifunctional derivatives with slight distortions due to steric factors. However, in three types of compounds the conformation is retained in one

[8] S. Wolfe, A. Rauk, L. M. Tel, and G. I. Csizmadia, *J. Chem. Soc.* (*B*), 1971, 136; S. Wolfe, *Accounts Chem. Res.*, 1972, **5**, 102.

function only, and reversed in the second (see Table 2). While the case of imido-carbonates[9] is easily understandable in terms of the strong steric hindrance of the asymmetric alkylimino-group, we feel that trithiocarbonates[10] should be studied in a more detailed manner. With dialkyl borinates the two possible planar forms are identical, so no prediction is possible regarding the alkyl boronates.

TABLE 2

Conformations around two equivalent bonds in non-polar solvents. Planar groups

X	Y	Monofunctional compound R–X–Y–R	Conformation around the X–Y bond (°)[a]	Bifunctional compound R–X–Y–X–R	Conformation around the two X–Y bonds (°)[a]	Symmetry	Relation of conformations[b]
O	CO	Ester[c]	180	Carbonate[d]	180, 180	C_{2v}	Retained
					or *ca.* 180, *ca.* 180	C_2	Very slightly distorted
S	CS	Dithioester[e]	180	Trithiocarbonate[f]	180, 180	C_{2v}	Retained
					and 0, 180	C_s	Retained in one group
O	C=NR	Imidate[g]	180	Imido-carbonate[h]	0, 180	C_s	Retained in one group
CO	O	Ester[c]	180	Anhydride[i]	*ca.* 160, *ca.* 160	C_2	Slightly distorted
CO	S	Thiolester[e]	180	Thioanhydride[l]	*ca.* 160, *ca.* 160	C_2	Slightly distorted
CO	NH	*N*-Alkylamide[m]	180	Diacylamide[n]	0, 180	C_s	Retained in one group
O	B(R)	Dialkyl borinate[o]	$0 \equiv 180$	Alkyl boronate[p,q]	0, 180	C_s	(Retained)

[a] The dihedral angles $\tau = \text{C}-\widehat{\text{X}-\text{Y}}-\text{C}$, or $\text{C}-\widehat{\text{X}-\text{Y}-\text{X}}-\text{C}$, respectively, are given; their direction is shown in Newman projections (A)—(D). [b] The conformation of the bifunctional compound in relation to that of the monofunctional compound. [c] See ref. 2*b*. [d] M. Yasumi, *J. Chem. Soc. Japan*, 1939, **60**, 1208; B. Collingwood, H. Lee, and J. K. Wilmshurst, *Austral. J. Chem.*, 1966, **19**, 1637. [e] See ref. 2*a*. [f] See ref. 10. [g] H. Lumbroso and D. M. Bertin, *Bull. Soc. chim. France*, 1970, 1728; O. Exner and O. Schindler, *Helv. Chim. Acta*, 1972, **55**, 1921. [h] See ref. 9. [i] See ref. 1*b*. [l] This work. [m] C. N. R. Rao, K. G. Rao, A. Goel, and D. Balasubramanian, *J. Chem. Soc.* (*A*), 1971, 3077; A. Kotera, S. Shibata, and K. Sone, *J. Amer. Chem. Soc.*, 1955, **77**, 6183. [n] G. Tóth, *Acta Chim. Acad. Sci. Hung.*, 1970, **64**, 101; T. Uno and K. Machida, *Bull. Chem. Soc. Japan*, 1962, **35**, 1226. [o] Not known from experiments, all the possibilities given are identical. [p] H. Lumbroso and A. Grau, *Bull. Soc. chim. France*, 1961, 1866. [q] See ref. 1*d*.

TABLE 3

Conformations around two equivalent bonds in benzene solution unless otherwise noted. Nonplanar groups

X	Y	Monofunctional compound R–X–Y–R	Conformation around the X–Y bond (°)[a]	Bifunctional compound R–X–Y–X–R	Conformations around the two X–Y bonds (°)[a]	Symmetry	Relation of conformations[b]
SO_2	O	Sulphonate[c]	$60 \equiv 300$	Sulphonic anhydride[d]	60, 300	C_2	Retained
					and 60, 60	C_s	Retained
SO_2	S	Thiosulphonate[e,f]	$60 \equiv 300$	Sulphonic thio-anhydride[d]	60, 300	C_2	Retained
					and 60, 60	C_s	Retained
O	SO	Sulphinate[g]	60	Sulphite[h]	60, 60 (?)	C_s	Retained
O	SO_2	Sulphonate[c]	$60 \equiv 300$	Sulphate[h]	60, 300	C_2	Retained
P(S)R	S	Dialkyl dithiophosphinate[i]	60 and 180 $\equiv$ 180 and 300[l]	Bisdialkylthiophosphinyl sulphide[l]	60 and 180 180 and 300[l]	C_2	Retained
O	P(O)R	Dialkyl phosphinate[m]	60[n]	Alkylphosphonate[o]	60, 60 (?)	C_s	Retained
O	CR_2	Ether[p]	$60 \equiv 180 \equiv 300$	Acetal[q,r]	60, 300	C_2	(Retained)
S	CR_2	Sulphide[p]	$60 \equiv 180 \equiv 300$	Dithioacetal[s–u]	60, 180	C_1	(Retained)
					and 60, 300	C_2	(Retained)
SO_2	CR_2	Sulphone[p]	$60 \equiv 180 \equiv 300$	*gem*-Disulphone[s]	60, 300	C_2	(Retained)
					and 60, 60 (?)	C_s	(Retained)
S	S	Disulphide[v]	$84 \equiv 276$	Trisulphide[w]	93, 267	C_2	(Retained)

[a,b] See Table 2. [c] See ref. 2*b*. [d] This work. [e] See ref. 2*c*. [f] See ref. 3. [g] O. Exner, P. Dembech, and P. Vivarelli, *J. Chem. Soc.*, (*B*), 1970, 278. [h] V. Jehlička and O. Exner, *Coll. Czech. Chem. Comm.*, in preparation. [l] See ref. 1*e*. [i] The two values are related to the two alkyl group present. [m] O. Exner and V. Jehlička, unpublished results; B. A. Arbuzov, P. R. Arshinova, O. A. Raevskii, and A. N. Vereshchagin, paper presented at the 5th All-Union Conference on Organophosphorous Compounds, Moscow, 1972. [n] Related to that alkyl group which is subsequently replaced by OR, the non-equivalence is induced by the position of the P=O bond. [o] E. A. Ishmaeva, A. N. Vereshchagin, N. A. Bondarenko, and A. N. Pudovik, *Izvest. Akad. Nauk S.S.S.R.*, 1970, 2695. [p] Not known from experiments, all the possibilities are identical. [q] See ref. 1*a*. [r] E. E. Astrup, *Acta. Chem Scand.*, 1971, **25**, 1494. [s] See ref. 1*c*. [t] See ref. 6*a*. [u] See ref. 12. [v] M. J. Aroney, H. Chio, R. J. W. Le Fèvre, and D. V. Radford, *Austral. J. Chem.*, 1970, **23**, 199; B. Beagley and K. T. McAloon, *Trans. Faraday Soc.*, 1971, **67**, 3216. [w] In the gas phase and in crystal, J. Donohue, *J. Amer. Chem. Soc.*, 1950, **72**, 2701; J. Donohue and V. Schomaker, *J. Chem. Phys.*, 1948, **16**, 92.

(2) When the conformation of both X and Y is tetrahedral (including the lone electron pairs), the monofunctional model compound R–X–Y–R can exist in two staggered conformations, *viz. trans* ($\tau = 180°$) or *gauche* ($\tau = 60°$). The latter possibility is usually preferred, owing to the '*gauche*-effect'.[8] For the bifunctional compound four main conformations, (H)—(L), are possible. Their number increases if the group Y is nonsymmetrical. Table 3 reveals that the conformation of simple compounds is retained in all known cases. Only when Y = CR_2 are all conformations of the simple model

[9] D. Leibfritz and H. Kessler, *Chem. Comm.*, 1970, 655.

[10] P. Rosmus, R. Mayer, K. Herzog, and E. Steger, *Tetrahedron Letters*, 1967, 4495.

compounds (ethers, sulphides, sulphones) identical, and no comparison is possible.* Symmetric C_2 forms are preferred in this case. Moreover, the C_2 forms are preferred to C_s, or at least predominate in all cases in which the two possibilities are otherwise equivalent. In the case of nonsymmetrical Y groups (sulphinates, alkyl phosphonates), these two possibilities are not equivalent since the positions with $\tau = 60$ and 300° are not identical. Therefore, the C_s conformation is required in order to maintain the conformation of monofunctional compounds in each group. The general preference for the C_2 conformation can be understood in terms of electrostatic or steric interactions as well. In both cases the repulsive forces are greater between the pairs (A–A) and (B–B) than between two pairs (A–B), while the electrostatic attractive forces are smaller.† The only apparent exception to this rule is the nonsymmetrical conformation (K) of dithioacetals, where even equivalent groups are in non-equivalent positions.[1c,6a,12] An explanation is not available at present, but the asymmetry of the group Y in a number of compounds investigated[1c,6a] (Y = CHPh) may also play some role.

Up to now it has been assumed that the groups X are either monoatomic or achiral. In this case, only the C_2 conformations of the molecules R–X–Y–X–R are chiral and the compounds represent a racemic mixture. Their resolution would generally not be possible, since the antipodes (and also the C_s form) are interconvertible by rotation around single bonds. When the groups X were chiral, the compound R–X–Y–X–R existed as one racemic and one *meso*-form, both in nine conformations at the most.

In conclusion, we are able to state that conformation around two bonds attached to a common central atom can be predicted with high probability from the conformation of the corresponding monofunctional compounds. When the prediction is ambiguous, the conformation C_2 is preferred to C_s. Moderate steric and/or electrostatic effects cause a slight distortion, if any. These rules may serve as a starting point to discuss the conformation of complex molecules and to explain the possible exceptions. Of course, our examples have been restricted to simple compounds; particularly when alkyl groups are replaced by more complex functions, the conformation could be affected by their interaction (*e.g.* in acylals[5]). Also, when three equivalent bonds are involved, the conformations around them seem to undergo a much stronger mutual influence (*e.g.* in alkyl phosphates[13]). On the other hand, one can forecast that bonds separated by more than one atom will behave almost independently.

EXPERIMENTAL

Di-p-*toluoyl Sulphide* (2).—This compound was prepared from *p*-methylbenzoyl chloride following the procedure described[14] for the syntheses of dibenzoyl sulphide (1) and its *p*-dichloro-derivative (3). The *sulphide* (2) was formed in 87% yield, m.p. 83—84° (from ligroin) (Found: C, 71·2; H, 5·3; S, 11·8. $C_{16}H_{14}O_2S$ requires C, 71·1; H, 5·2; S, 11·9%).

p-*Chlorobenzenesulphonic Anhydride* (6).—This was obtained in 75% yield by reaction between *p*-chlorobenzenesulphonic acid and phosphorous pentoxide as described[15] for the syntheses of compounds (4) and (5). It had m.p. 151—152° (from dry benzene–diethyl ether) (Found: C, 39·6; H, 2·2; Cl, 19·5; S, 17·3. $C_{12}H_8Cl_2O_5S$ requires C, 39·3; H, 2·2; Cl, 19·3; S, 17·5%).

p-*Chlorobenzenesulphonic Thioanhydride* (9).—This was obtained in 58% yield starting from the silver salt of *p*-chlorobenzenesulphinic acid by the procedure described[16] for the syntheses of compounds (7) and (8). It had m.p. 119—120° (from ligroin) (Found: C, 37·5; H, 2·1; Cl, 18·4; S, 25·3. $C_{12}H_8Cl_2O_4S_3$ requires C, 37·6; H, 2·1; Cl, 18·5; S, 25·1%).

The solvents employed were AnalaR commercial products carefully dried by standard methods.[17]

Physical Measurements.—These were carried out in benzene at 25° by the procedure previously described.[2b,5]

Dielectric constants and densities were measured by Mrs. M. Kuthanová, Department of Physical Chemistry, Institute of Chemical Technology, Prague, under the supervision of Dr. V. Jehlička. Their aid is gratefully acknowledged. Thanks are due to Mrs. S. Rossini for her contribution to the synthetic work.

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* In this case, as well as in some others, the halogen compounds R–X–Y–Hal may represent a better model. For acetals they would yield the correct prediction; however, the conformations of other similar classes of compounds, or even these compounds themselves, are not known. We thank Dr. A. N. Vereshchagin, Kazan, for discussions on this point.

† When lone electron pairs are involved, their electrostatic interaction also disfavours the C_s form; this has been called[11] the 'rabbit-ear effect.' In our opinion it is only a particular case of the more general phenomenon and does not deserve this special name.

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