DIPOLE MOMENTS AND SOLUTION CONFORMATION
OF SUBSTITUTED DIBENZOYL PEROXIDES

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Dipole moments of dibenzoyl peroxide and its 4,4'-bisderivatives in solution allow to confirm unambiguously the C_2 conformation *I*, found in the crystalline state. In order to reach a perfect agreement between calculated and experimental values, certain deviations from the solid state geometry must be assumed; probably there are slight changes in the bond angles rather than in the dihedral angle C—O—O—C. In the case of 3,3'- and 2,2'-bisderivatives three conformations with the benzene rings coplanar to the adjacent functional group are possible (*IIa*—*IIc*); their ratio seems to be slightly different from the statistical representation.

In connection with the recent work on peroxides[1] we were also interested in the dipole moments of aromatic diacyl peroxides and their conformation in solution. In the crystalline state[2] dibenzoyl peroxide is known to possess a C_2 conformation (*I*) with the dihedral angle $\tau = \sphericalangle$ C—O—O—C of 91°, while the two benzene nuclei are virtually coplanar, each with its neighbouring COO group. In 4,4'-dichloro and dibromo derivatives the dihedral angles are somewhat less[3], 84° and 81°, respectively. In solution, essentially the same conformation was deduced from IR spectra[4] and first even from dipole moments[5]. The latter study was confined to dibenzoyl peroxide, its 4,4'-dichloro derivative and several aliphatic diacyl peroxides. The discussion of conformation was complicated by taking into consideration different possible forms even for the COO groups themselves; as the final result the dihedral angle τ was estimated to 100°.

In the present study we have investigated first of all several 4,4'-bisderivatives of dibenzoyl peroxide (Table I) with the aim to obtain more information concerning the dihedral angle τ, its constancy in various derivatives, and the more detailed geometry of the COO groups. The Z conformation on the C—O bond of these groups (like in *I*) was not doubted with respect of the uniform conformation of esters and all other compounds containing the COO group[6]. Further we dealt with the corresponding 3,3'- and 2,2'-derivatives (Table I) for which three conformations (*IIa*—*IIc*) are possible as far as the coplanarity of each benzene nucleus with the adjacent COO group is to be maintained. The dipole moments should decide whether

the representation of these conformations is a statistical one, or inasmuch it is controlled by electrostatic interactions. The selection of compounds investigated was somewhat restricted by their solubility since we intended to compare all data in one solvent (benzene).
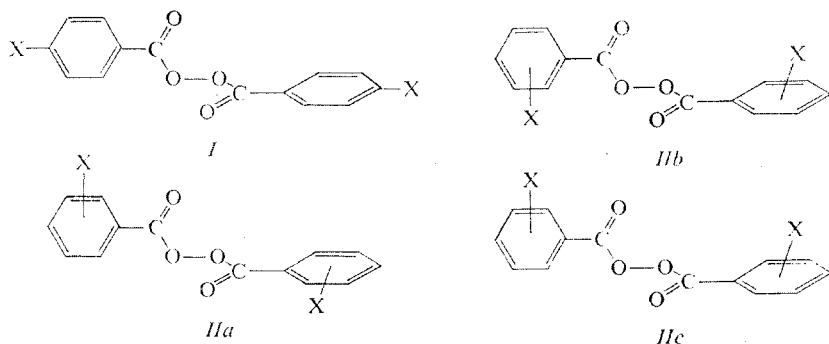
EXPERIMENTAL AND RESULTS

Materials. Substituted dibenzoyl peroxides were prepared by known procedures[7]. The identity of each compound was checked by usual physical and chemical methods. All specimens were found to be over 99% pure.

The ^{1}H NMR spectra were obtained with a JEOL JNM—C—60 HL spectrometer (CDCl$_3$ solution, tetramethylsilane as internal standard).

Measurement of dipole moments: The same method was used as in previous work[8,9]. Molar refractions were calculated from Vogel's increments[10] and an exaltation of 0·7 cm^3 added for each conjugation C$_6$H$_5$—CO; the calculated values agreed but fairly with those determined in solution[5] for two compounds of our set. The dipole moments and the auxiliary data are listed in Table I.

DISCUSSION

As the first step of the interpretation an attempt was made whether the solution conformation may be determined — at least in its essential features — from the present data alone. The expected dipole moments were computed for varying values of the dihedral angle τ, using bond angles essentially equal to those determined in the crystalline state[2] ($\sphericalangle$ C—C=O = 127°, $\sphericalangle$ C—C—O = 110°, $\sphericalangle$ C—O—O = = 110°), and bond moments well-tried in previous work[8,9] (C=O 2·5 D, C—O 0·74 D, H—C$_{al}$ 0·3 D, H=C$_{ar}$ 0 D, C$_{ar}$—Cl 1·6 D, C$_{ar}$—Br 1·58 D, C$_{ar}$—F 1·35 D, C$_{ar}$—NO$_2$ 4·0 D). The mesomeric dipole moment for the conjugation C$_6$H$_5$—CO was taken to be 0·25 D but its value is virtually irrelevant. The calculated values are

compared with the experimental ones using the graphical method[9] (Fig. 1, broken line). The following conclusions are evident: *a*) A non-planar C_2 conformation is proven. *b*) The dihedral angle τ would be estimated to 115° compared with the crystallographic value[2] of 91°. Alternatively, assuming that the latter value is maintained in solution, the calculated dipole moments are all too low. *c*) The experimental dipole moments of all 4,4'-bisderivatives are significantly lower compared with the unsubstituted compound, whereas according to the calculation they should be equal.

The generally too low calculated moments (see ad *b*) could be also understood by an improper choice of bond moments, *e.g.* the polarity of the C—O bond in diacyl peroxides need not be exactly equal as in esters. However, the difference between dibenzoyl peroxide and its derivatives (ad *c*) cannot be explained in such terms and two other explanations come merely into consideration: Either is the dihedral angle τ variable, *viz* dependent on substitution, or the geometry of the acyl groups is different from that in the crystalline state, but constant. We hold the former possibility to be less probable. The necessary variance of τ would be from 108° in dibenzoyl peroxide to 126° in 4,4'-difluorodibenzoyl peroxide. These generally too high values might be lowered by adjusting properly the bond moments, but their variability is in any case too large with respect to a remote substitution. The X-ray studies revealed a smaller

TABLE I

Dipole Moment Data of Substituted Dibenzoyl Peroxides (Benzene, 25°C)

Substituents	P_2^0 cm^3	R_D^{20a} cm^3	$\mu\ (5\%)^b$ D	$\mu\ (15\%)^b$ D	$\mu_{calc}{}^d$ D
H	121·6	64·5	1·62^d	1·52	1·52
2,2'-F$_2$	162·7	64·1	2·16	2·09	2·38
2,2'-Cl$_2$	202·9	74·4	2·47	2·39	2·52
2,2'-Br$_2$	182·2	80·1	2·19	2·10	2·52
3,3'-Cl$_2$	182·6	74·4	2·26	2·18	2·39
3,3'-Br$_2$	180·7	80·1	2·17	2·08	2·39
3,3'-(NO$_2$)$_2$	560·3	77·2	4·78	4·75	5·01
4,4'-F$_2$	100·3	64·1	1·27	1·14	1·33
4,4'-Cl$_2$	117·3	74·4	1·38^e	1·25	1·30
4,4'-Br$_2$	123·8	80·1	1·39	1·25	1·30
4,4'-(CH$_3$)$_2$	138·7	73·8	1·73	1·62	1·55

[a] Calculated from increments as described in the Experimental part; [b] correction for the atomic polarization 5%, or 15% of the R_D value, respectively; [c] calculated for the dihedral angle C—O——O—C 91° and the statistical representation of rotamers *IIa* — *IIc*, the bond moments were given in the Discussion; [d] ref.[5] gives 1·60 D (30°C, 0% correction); [e] ref.[5] gives 1·33 D (30°C, 0% correction).

difference betweeen the dihedral angles in dibenzoyl peroxide[2] and its 3,3'-dichloro and dibromo derivatives[3] but just in the opposite direction.

On the other hand, a slight change of the geometry of the two COO groups can account for the observed facts when the bond angles $\measuredangle$ C—C—O $= 109°$ and $\measuredangle$ C—O—O $= 114°$ are adopted. These values differ only by $1°$ or $4°$, respectively, from the X-ray values[2], moreover the latter corresponds better to the geometry of common esters. To get a perfect agreement of experimental and calculated dipole moments $\left(i.e.\text{ for the dihedral angle of } 91°\right)$, it is still necessary to amend the values of bond moments. The amendment should express the apparently greater electronegativity of the peroxide oxygen compared with the ether oxygen in esters, on which the bond moments have been verified. Formally this can be achieved by enhancing the C—O moment, or reducing the C=O moment, or by both. Usung the *a posteriori* adjusted values for C=O 2·3 D and C—O 1 D, we calculated the expected dipole moments plotted in Fig. 1 (full line). Of course, the result must accord with the dihedral angle of $91°$ from which it was derived. An actual test is obtained by calculating the expected values for all the 4,4'-bisderivatives of Table I; these are listed in the last column and agree reasonably with the general trend as well as with the individual experimental values.

In the case of 3,3'-bisderivatives, the three conformations $(IIa-IIc)$ may be assumed to be represented statistically, *i.e.* in the ratio 1 : 1 : 2, at least in the first approximation. However, a detailed dipole moment study[11] of 3-chloro derivatives of benzaldehyde, acetophenone *etc.* revealed a slight predominance $(53-59\%)$ of the *trans* conformer in each case; this was explained by electrostatic forces. Although the precision of the approach has been overestimated[11] in our opinion,
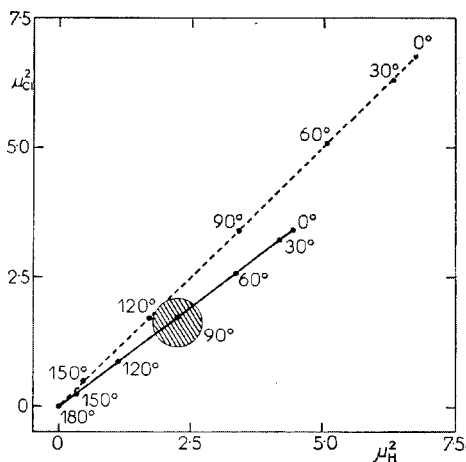

FIG. 1

Comparison of Squared Dipole Moments of Dibenzoyl Peroxide (x axis) and Its 4,4'-Dichloro Derivative (y axis)

Broken line values calculated for the solid state geometry and with standard bond moments, full line improved geometry as well as bond moments, shadowed circle — experimental values.

the generality of the results grants them credit. Our present findings are also in ac-
cord: We calculated the expected dipole moments for the statistical mixtures with
otherwise the same assumptions as used for the 4,4′-bisderivatives. The calculated
values (Table I) are slightly but uniformly higher than the experimental ones, showing
that the *trans–trans* form *IIb* with the lowest dipole moment is somewhat more
abundant. We do not dare to express this abundance numerically with respect
to many assumptions and approximations inherent in the whole procedure.

Similar considerations apply to 2,2′-bisderivatives; the electrostatic effect should be
much stronger and in addition some purely steric factors could come into play.
The actual results are, however, the same as for 3,3′-derivatives.

The interconversion of rotamers *IIa−IIc* is expected to be very easy since the
barriers to rotation about the C—C_{ar} bond are generally low. Actually the ^{1}H-NMR
spectra of 2,2′- and 3,3′-dimethyldibenzoyl peroxide revealed only one signal of methyl
protons $(\delta\ 2\cdot60$ and $2\cdot37$, respectively) between $-50°C$ and $+40°C$. Summarizing
we can state that the slight predominance of the *trans–trans* form *IIb* agrees qualita-
tively with the electrostatic theory but the effect is too small to be viewed as its
experimental support.

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