DIPOLE MOMENTS AND CONFORMATION OF PEROXY ESTERS*

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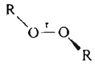
Dipole moments of sixteen substituted peroxybenzoic esters *III*, *IV* were measured in benzene solution and interpreted in terms of the conformation around the O—O bond. The dipole moment of the CO_3R group is different for R = methyl and R = tert-butyl, *viz.* 9·0 and 10·4 . 10^{-30} C m, respectively. Its resolution into components was carried out making reference to the dipole moments of substituted benzoic esters as model compounds. As a result the dihedral angle τ = C—O—O—C was estimated to 160—180° in the case of tert-butyl peroxy esters *IV* and to 110—150° in the case of methyl peroxy esters *III*.

The mesomeric dipole moment expressing the conjugation within the ester group was estimated to 0·8 or 1·5 . 10^{-30} C m for methyl or tert-butyl esters, respectively.

The stereochemistry of organic peroxy compounds *I*–*IV* is dominated by the conformation around the O—O bond. Since the potential energy curve is usually flat, the dihedral angle τ = C—O—O—C varies in different compounds and at different conditions. On the other hand, the instability of many of the compounds has prevented them from being studied in the gas phase or even in crystal. For these reasons the dipole moment measurement in solution has proven to be an important approach in spite of its rather limited accuracy. It revealed the non-planar conformation of dialkyl peroxides *I* with τ estimated to 123 – 126° for di-tert-butyl peroxide[1–3], and of diacyl peroxides[2,4] *II* with τ approximately 90° (in benzene) while the pertinent value for di-tert-butyl peroxide in the gas phase[5] is 166°. The parent compound, hydrogen peroxide, has a conformation with τ = 120° in the gas phase[6] and with 90° in crystal[7].



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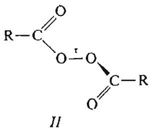

II

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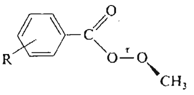
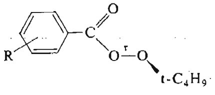
* Part IV in the series Mesomeric Dipole Moments; Part III: This Journal *45*, 2410 (1980).

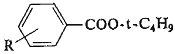


III; *a*, *b*, see Table I



IV; *a*—*h*, see Table I

The unsymmetrical derivatives, peroxy esters *III*, *IV* present a more difficult problem since the range of anticipated dipole moment values arising by rotation around the O—O bond is more narrow, from 5 to 10 instead of from zero to 7 or to 9 in the case of compounds *I* and *II*, respectively. (All dipole moment values are given in the units 10^{-30} C m.) This is one reason why a previous attempt[8] to determine the conformation of *IV* was not successful, resulting in three possible solutions; as the most probable a conformation with the angle τ between 10 and 150° and with a slightly non-planar carboxy group was claimed. There is, however, an ample evidence[9] that the carboxy group is planar – within the accuracy of several methods – in esters of various types. In our opinion, the most important shortcoming of the paper quoted[8] is the restriction to aliphatic and unsubstituted aromatic compounds; without any polar substituent the dipole moments are not sufficiently different and two unknown geometrical parameters cannot be estimated from one experimental number. On the contrary, the present study is based only on aromatic peroxy esters (Table I) bearing substituents with defined bond and group moments[10]. Comparison of experimental and calculated moments was made using the well-tried graphical representation[11]. Since the methyl peroxy esters *III* are mostly insufficiently stable, we preferred tert-butyl peroxy esters *IV* like the previous authors[8]. In order to estimate a possible effect of the tert-butyl group, we undertook a comparative study of aromatic tert-butyl esters *Va*–*f* (Table I) as model compounds. At this opportunity the problem of the mesomeric effect within the ester group[12,13] was reinvestigated. Our approach is thus restricted to aromatic derivatives and we cannot ascertain whether the aliphatic ones possess exactly the same conformation.



V; *a*—*f*, see Table I

TABLE I

Polarization and Dipole Moments of Substituted Peroxybenzoates and Benzoates (25°C)

Compound	Solvent	α[a] β[a]	P_2^0, cm^3 R_D[b], cm^3	μ(5)[c] μ(15)[c]	μ_{calc}[d]
$4\text{-ClC}_6\text{H}_4\text{CO}_3\text{CH}_3$	Bz	2·84	150	7·5	7·3[e]
IIIa		—0·238	45·9	7·3	
$4\text{-NO}_2\text{C}_6\text{H}_4\text{CO}_3\text{CH}_3$	Bz	6·33	277	11·2	11·0[e]
IIIb		—0·420	47·3	11·1	
$\text{C}_6\text{H}_5\text{CO}_3\text{—t-C}_4\text{H}_9$	Bz	6·02	274	10·9[f]	10·2[g]
IVa		—0·211	54·9	10·8	
$4\text{-CH}_3\text{C}_6\text{H}_4\text{CO}_3\text{—t-C}_4\text{H}_9$	Bz	5·59	267	10·6	10·8[g]
IVb		—0·370	58·6	10·5	
$3\text{-ClC}_6\text{H}_4\text{CO}_3\text{—t-C}_4\text{H}_9$	Bz	4·17	239	9·8	10·4[g,h]
IVc		—0·268	59·9	9·7	
$4\text{-ClC}_6\text{H}_4\text{CO}_3\text{—t-C}_4\text{H}_9$	Bz	4·57	256	10·3	9·0[g]
IVd		—0·273	59·9	10·1	
$3\text{-BrC}_6\text{H}_4\text{CO}_3\text{—t-C}_4\text{H}_9$	Bz	3·00	213	8·9	10·4[g,h]
IVe		—0·416	62·8	8·8	
$4\text{-BrC}_6\text{H}_4\text{CO}_3\text{—t-C}_4\text{H}_9$	Bz	3·12	241	9·8	9·0[g]
IVf		—0·155	62·8	9·6	
$3\text{-NO}_2\text{C}_6\text{H}_4\text{CO}_3\text{—t-C}_4\text{H}_9$	Bz	7·62	402	13·6	14·7[g,h]
IVg		—0·312	61·3	13·5	
$4\text{-NO}_2\text{C}_6\text{H}_4\text{CO}_3\text{—t-C}_4\text{H}_9$	Bz	6·51	351	12·5	12·3[g]
IVh		—0·331	61·3	12·4	
$\text{C}_6\text{H}_5\text{CO}_2\text{—t-C}_4\text{H}_9$	Bz	2·45	135	6·6	6·5[j]
Va		—0·147	51·9	6·4	
	Diox	3·20	145	7·0	
		0·022	51·9	6·8	
$4\text{-CH}_3\text{C}_6\text{H}_4\text{CO}_2\text{—t-C}_4\text{H}_9$	Bz	2·67	154	7·2	6·8[j]
Vb		—0·134	56·5	7·0	
	Diox	3·34	161	7·5	
		0·030	56·5	7·2	
$3\text{-ClC}_6\text{H}_4\text{CO}_2\text{—t-C}_4\text{H}_9$	Bz	2·59	160	7·4	7·8[h,j]
Vc		—0·256	56·8	7·2	
	Diox	3·33	171	7·8	
		—0·086	56·8	7·6	
$4\text{-ClC}_6\text{H}_4\text{CO}_2\text{—t-C}_4\text{H}_9$	Bz	2·67	163	7·5	7·2[j]
Vd		—0·253	56·8	7·3	
	Diox	3·16	165	7·6	
		—0·090	56·8	7·4	

TABLE I
(*Continued*)

Compound	Solvent	α^a β^a	P_2^0, cm^3 $R_D{}^b$, cm^3	$\mu(5)^c$ $\mu(15)^c$	$\mu_{calc}{}^d$
$3\text{-}BrC_6H_4CO_2\text{—t-}C_4H_9$	Bz	2·10	158	7·2	7·8^{h,j}
Ve		—0·406	59·7	7·0	
	Diox	2·70	169	7·6	
		—0·236	59·7	7·4	
$4\text{-}BrC_6H_4CO_2\text{—t-}C_4H_9$	Bz	2·14	162	7·4	7·2^j
		—0·383	59·7	7·1	
	Diox	2·79	173	7·8	
		—0·230	59·7	7·6	

[a] Slopes of the plots ε_{12} *vs* w_2 and d_{12}^{-1} *vs* w_2, respectively; [b] calculated from increments, see Experimental; [c] in units 10^{-30} C m, correction for the atomic polarization 5% or 15%, respectively, of the R_D value; [d] calculated from bond moments, see Experimental (units 10^{-30} C m); [e] dihedral angle C—O—O—C = 120°, mesomeric moment within the COO group 0·83; [f] ref.[8] gives 10·5 at 30°C; [g] dihedral angle C—O—O—C = 180°, mesomeric moment within the COO group 0·83, the O—t-C_4H_9 group moment enhanced to 4·13; [h] assuming equal population of the two coplanar conformations of the benzene ring; [j] mesomeric moment within the COO group taken as 1·5, the O—t-C_4H_9 group moment as 4·13.

EXPERIMENTAL

Materials. Methyl peroxybenzoates *III* were prepared as proposed by Brenner and coworkers[14]. The corresponding diaroyl peroxide was converted into the sodium salt of peroxybenzoic acid by the action of sodium methoxide in dichloromethane at —10°C, and subsequently alkylated with trimethyloxonium fluoroborate, yield 50—70%. Tert-butyl peroxybenzoates were prepared according to the literature[15]. All peroxybenzoates investigated were found to be over 98% pure by iodometry. Tert-butyl benzoates *V* were obtained by the standard procedure[16]. All derivatives investigated in this paper are known compounds and their physical properties agreed with the literature.

Physical measurements. The procedure of measurement[17] and the properties of dioxan used as solvent[18] were reported recently. Even a slight decomposition of a compound in solution prevented to obtain reliable results and such measurements were omitted. The values of molar refraction for peroxy esters were based on the experimental determination on tert-butyl peroxybenzoate[8] (*IVa*) from which the values for the remaining compounds were calculated using standard increments[19]. The starting experimental value is unexpectedly high but this is not manifested in the final dipole moments. In calculating the molar refraction R_D for the esters *V* only an exaltation[20] of 0·7 cm^3 for the conjugation of the carboxyl group with the benzene nucleus was applied in addition to the standard increments[19]. The dipole moments and the auxiliary data are listed in Table I.

Calculations. The dipole moments assumed for individual conformations were calculated using the following set of standard bond moments[10] (10^{-30} C m): H—C_{al} 1, H–C_{ar} 0, C—O 2·47, C=O 8·33, C_{ar}—Cl 5·33, C_{ar}—Br 5·23, C_{ar}—NO_2 13·33, in addition a mesomeric correction of 0·83 for the conjugation C_6H_5—CO (m_1); another mesomeric moment (m_2) expressing the conjugation within the carboxy group will be discussed in the next part.

For the molecule of peroxy esters we used the bond angles: C—C=O 127°, O=C—O 124°, and C—O—O 114°, discussed previously[4], in addition the angle O—O—R 115°. For the ester molecule the standard values C—C=O 124°, and C—O—C 115° were applied. The final results are not sensitive to the uncertainty inherent in these quantities.

RESULTS AND DISCUSSION

Of the data in Table I let us consider first the five *para*-substituted tert-butyl peroxybenzoates (*IVa*, *IVb*, *IVd*, *IVf*, *IVh*) which may serve to derive the group moment CO_3—t-C_4H_9 from the known bond moments of the substituents (construction of a triangle). The coincidence of the results is quite good, considering the unstability of the compounds. The resulting vector has the value of 10·4 at an angle of 66° to the C(1)—C(O) bond. The measurements on the *meta* derivatives (*IVc*, *IVe*, *IVg*) are essentially in agreement with this group moment if equal populations of the two coplanar conformations are assumed. Nevertheless, this assumption might be only approximate since the calculated values (Table I, last column) are always somewhat higher than the experimental ones. In a similar way the group moment CO_3CH_3 can be estimated to 9·0 (57°) from the two methyl derivatives *IIIa*, *IIIb* but the uncertainty is of consequence. The direction of these vectors in space is not known; only if the functional groups were planar (τ = 0° or 180°), the vectors would be situated in its plane. In any case, however, the absolute values can be compared with the calculations from bond moments which are in the range between 5·0 for the *sp*-conformation

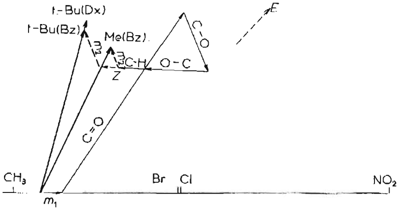


FIG. 1

The Dipole Moment of the COOR Group and Its Analysis into Components

Shown are experimental group moments for the COO—t-C_4H_9 group (in benzene and in dioxan) and for the $COOCH_3$ group (in benzene) by heavy arrows, the bond moments for the conformations *Z* and *E*, and the mesomeric corrections m_1 and m_2.

($\tau = 0°$) and 9·3 for the *ap*-conformation ($\tau = 180°$). The comparison suggests that the calculation with standard bond moments is not sufficiently precise for our purpose and we tried to refine it by referring to tert-butyl esters as model compounds.

The dipole moment data (Table I) of substituted tert-butyl benzoates *V* were processed in the same manner as in the preceding paragraph. Again the *para* derivatives were of deciding importance, but even the *meta* derivatives were in agreement. The group moment CO_2—t-C_4H_9 was found to be 6·5 or 6·8 in benzene or in dioxan, respectively, in any case at an angle of 74° to the C(1)—C(O) bond. Similarly we derived the value of 6·2 (64°) for the CO_2CH_3 group from the published data in benzene[21]. The latter value agrees with our previous estimate[13] and does not differ significantly from those tabulated by Minkin and coworkers[22], *viz.* 6·1 (70°) for methyl esters and 6·3 (62°) for ethyl esters. The experimental group moments are pictured in Fig. 1 and compared to the vector sum of bond moments. Evidently, only the *Z*-conformation comes into consideration but the agreement is not perfect. An improvement is possible through two additional mesomeric corrections. One of them (denoted m_1) expresses the conjugation of the functional group with the aromatic nucleus and is well substantiated by the comparison of aliphatic and aromatic esters. The other (m_2) corresponds to the conjugation within the ester group ($A \leftrightarrow B$) and has to be estimated from Fig. 1. Since it is certainly small and depends on all the bond moments introduced, there has been no agreement about its value and even about its necessity. We offered previously the opinion that it is not well evidenced[13], while in the literature[12,23] the estimates of 1·3 or 2·2 are reported; in either case the direction from the ether oxygen to the carbonyl oxygen was *a priori* assumed, as suggested by the mesomeric formulae $A \leftrightarrow B$. From Fig. 1 the value of $m_2 = 0·8$ can be inferred for methyl

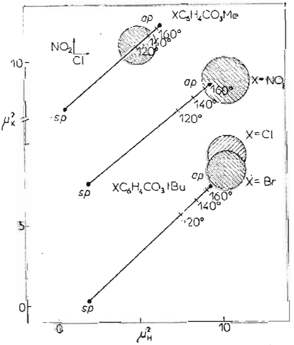


FIG. 2

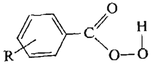
Comparison of Squared Dipole Moments of Peroxy Esters, Calculated and Experimental

Shown are experimental values by hatched circles, calculated values for varying angle τ by full points with their connecting lines; on the *x*-axis compounds *IIIa* and *IVa*, on the *y*-axis *IIIb*, *IVd*, *IVf*, *IVh*, respectively.

esters, its direction is, however, from the ether oxygen to carbon. There are, of course, doubts about the physical meaning of this small value but the comparison with amides[24] is encouraging in this respect. The mesomeric moment increases from esters (0·8) to amides (approximately 2) and N,N-dimethylamides (4·7) while its direction is the same in all the compounds, *i.e.* from N to C in the case of amides. Irrespective of its physical meaning the vector m_2 can be introduced as an empirical correction into the bond moment scheme. In the case of tert-butyl esters a greater value is necessary ($m_2 = 1·5$) which is understandable in terms of the enhanced basicity of oxygen and parallels the difference between amides and N,N-dimethylamides[24]. In addition, another minor correction is requisite: rising the R—O group moment by 0·7. This second correction is not easy to explain, it is *e.g.* just the opposite of what would be expected from a deformation of C—C—C bond angles. It is also not connected with solvent effects since the dipole moments in dioxan are very little changed. We will regard it as purely empirical for the present purpose.

A *B*

We can now return to the peroxy esters and recalculate the anticipated dipole moments with the above corrections. It means that the enhanced group moment was introduced in the case of tert-butyl derivatives *IV* but the mesomeric moment $m_2 = 0·8$ was applied for both *III* and *IV* since we believed that the remote tert-butyl group in *IV* cannot affect the mesomeric interaction in the same way as in *V*. The calculated values are compared with experiment in Fig. 2 and in the last column of Table I. The comparison reveals that the actual conformation is not far from planar, with τ near to 180°. Unfortunately, the dipole moments are little sensitive to changes of this angle just in this region so that even $\tau = 160°$ must be admitted for tert-butyl derivatives *IV* and the range of possible values for methyl derivatives *III* is approximately from 110° to 150°. Compared with the previous study[8] our results are somewhat more definite, the angle τ found by us is larger and last but not least we assume



VI

no deformation of the carboxy group. With the large value of τ the conformation of peroxy esters is entirely different from that of the parent peroxy acids *VI* which is controlled by an intramolecular hydrogen bond[18,25]. A common feature of both compounds might be, however, a flat potential energy curve since the angle τ in *VI* can attain as much as 170° in the crystalline state[26] when the intramolecular hydrogen bond is replaced by an intermolecular one.

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