

THE CONFORMATION OF ARYL CARBONATES. A DIPOLE MOMENT STUDY

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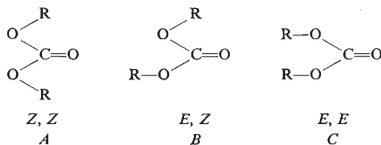
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The dipole moments of diaryl carbonates *I*–*V* in benzene solution are consistent with the *Z,Z*-conformation (*A*) in which the conformation of simple esters is repeated in the two moieties. The *E,Z*-form (*B*) was not detected; it may be either present as a quite small fraction or only with specific, overcrowded structures.

The conformation of the title compounds is a particular case of a broader problem we have been approaching by the dipole moment method^{1–4}, viz. the conformation around two equivalent single bonds linked to one central atom. Two simple rules were suggested⁵: 1) The conformation of the corresponding monofunctional compound is repeated in each moiety of the bifunctional derivative unless it is prevented by a strong steric hindrance. 2) Symmetrical conformations are generally favoured; if there are two possibilities, then the C_2 symmetry has preference to C_s . For diesters of carbonic acid only the rule (1) is operative and predicts the *Z,Z*-conformation (*A*), which corresponds to simple esters⁶ but is sterically more crowded than *E,Z* (*B*):



The form *A* is actually present in crystals of bis(trichloromethyl) carbonate⁷ and was inferred from dipole moments of dialkyl carbonates both in the gas phase⁸ and in solution⁹; informative is the comparison with ethylene carbonate^{10,11} having the fixed conformation *E, E* (*C*). The IR spectrum of dimethyl carbonate in the gaseous state was interpreted in terms of conformation¹² *A*, possibly slightly distorted¹³

(C_2 symmetry) while in the liquid the presence of another conformer, probably *B*, was claimed¹⁴. All these results were challenged by Oki and Nakanishi¹⁵ who believe that the form *B* (possibly not quite planar) is strongly populated with all carbonates and mostly even prevails; some evidence was in fact presented only for methyl tert-butyl carbonate and similar overcrowded derivatives. This general claim was criticized^{12,14} but the conformation *B* was recognized¹² in the case of di-tert-butyl carbonate.

We were of the opinion that the dipole moment measurement can contribute significantly to the problem if — in contradistinction to previous work^{8-11,15} — advantage is taken of introducing polar substituents. Therefore, we investigated the aromatic derivatives *I-V* (Table I) and evaluated the results by the well-tried graphical method¹⁶. Our intention was to establish the conformation of aromatic carbonates, hitherto little studied¹⁵, and to get possibly some indirect evidence concerning the other derivatives.

TABLE I
Polarization Data of Diaryl Carbonates (benzene, 25°C)

No	Compound	M.p., °C	$\frac{\alpha^a}{\beta^a}$	P_0 R_D cm ³	$\frac{\mu(5\%)^c}{\mu(15\%)^c} 10^{-30}$ Cm
<i>I</i>	(C ₆ H ₅ O) ₂ CO	79	0.95	93.1	4.1 ^d
			-0.286	59.3	3.7
<i>II</i>	(4-CH ₃ C ₆ H ₄ O) ₂ CO	113	0.64	94.7	3.5
			-0.238	68.7	2.9
<i>III</i>	(4-ClC ₆ H ₄ O) ₂ CO	151	1.03	112.3	4.7 ^d
			-0.463	69.1	4.2
<i>IV</i>	(4-NO ₂ C ₆ H ₄ O) ₂ CO	140	12.57	781	19.6 ^e
			-0.455	72.7	19.5
<i>V</i>	(1-C ₁₀ H ₇ O) ₂ CO	130	1.23	146.9	5.1 ^f
			-0.352	94.8	4.5

^a Slopes of the plots ϵ_{12} vs w_2 and v_{12}^{-1} vs w_2 , respectively; ^b calculated from increments²⁴, valid for 20°C; exaltations of 0.3 cm³ were added for each O—C₆H₅ conjugation and in addition 0.4 cm³ for each conjugation NO₂—C₆H₄—O (the latter is quite insignificant due to the large dipole moment of the nitro derivative *III*); the increment of 1-naphthyl see²⁵; ^c correction for the atomic polarization 5% or 15% of the R_D value, respectively; ^d these figures are more reliable than 2.2 and 4.3 · 10⁻³⁰ Cm, as given for *I* and *III* respectively, in the Thesis²⁶; ^e in agreement with ref.²⁶; ^f the values of ref.²⁶ are in error.

EXPERIMENTAL

Diaryl carbonates *I-IV* (Table I) were prepared from the respective sodium phenolate and phosgene in toluene solution¹⁷, di-1-naphthyl carbonate (*V*) was made available to us from the collection of the Institute of Chemical Technology, Pardubice. The melting points agreed with the literature¹⁷⁻²¹. The technique of dipole moments measurement was described in some detail²².

Theoretical dipole moments, anticipated for conformations *A-C*, were calculated from standard bond moments²³ (10^{-30} Cm): $H-C_{al}$ 1, $H-C_{ar}$ 0, $C=O$ 8.33, $C-O$ 2.47, $C_{ar}-Cl$ 5.33, $C_{ar}-NO_2$ 15.0 (including the conjugation with a *para*-standing oxygen), the bond angles used were $O=C-O$ 125° and $O-C-O$ 113°. (The angles in bis(trichloromethyl) carbonate⁷ are not typical since they are evidently broadened by the strong repulsion between the carbonyl oxygen and chlorine atoms.) The calculated dipole moments are plotted in Figs 1 and 2.

RESULTS AND DISCUSSION

Our results illustrated in Figs 1 and 2 are in agreement with the *Z,Z*-conformation *A* and do not yield any support either for its supposed distortion (see the full curves

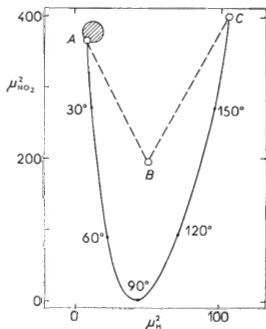


FIG. 1

Comparison of Squared Dipole Moments of Diaryl Carbonates *I* and *IV*, Calculated and Experimental

Empty points — calculated for the conformations *A-C*; full curve — C_2 -conformations intermediate between *A* and *C* (the dihedral angle $O=C-O-C$ is given); broken straight lines — mixtures of the conformations *A* and *B*, or *B* and *C*, respectively; hatched circle — experimental values.

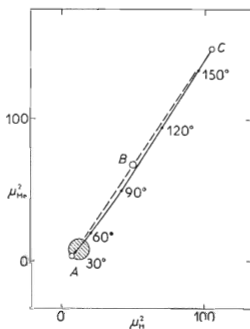


FIG. 2

Comparison of Squared Dipole Moments of Diaryl Carbonates *I* and *II*

See Fig. 1 for descriptive details.

in the Figs 1 and 2) or for the presence of form *B* (the direction of the broken straight lines). Note that the precision of the approach is limited, in particular the small dipole moments of *I* and *II* are determined with a large relative uncertainty because the correction for atomic polarization is of significant importance. These values are somewhat larger than calculated for the form *A*. In our graphical representation, however, the values of μ^2 are plotted so that a true picture of the variable accuracy is obtained. It follows that the nitro derivative *IV* is of decisive importance among our compounds, illustrating once again the significance of proper substitution in dipole moment work. Our conclusions may be worded that the same conformation was found for diaryl carbonates as previously for the aliphatic derivatives⁷⁻¹⁴. It agrees also with the *ab initio* calculations on the simplest model compound carbonic acid²⁷ — at least in a qualitative sense.*

The dipole moment of *III* seems too low as compared to the calculated value of $8.56 \cdot 10^{-30}$ C.m corresponding to the conformation *A*. This anomaly is not without precedence, compare the low dipole moment of 4-chlorophenyl acetate²⁹. In general, however, the 4-chloro substituent is well-trying in dipole moment work since it does not interfere with *para*-standing groups. The dipole moment of *V*, enhanced with respect to *I*, may be due to steric crowding. It follows that the determination of conformation is actually based on the nitro derivative *IV* on the one hand, and on the two similar low moments of *I* and *II* on the other.

As regards the possible presence of the *E,Z*-form (*B*), it is in our opinion not sufficiently evidenced. Diphenyl carbonate exhibits three not well resolved maxima of the carbonyl band, one of which was tentatively assigned¹⁵ to Fermi resonance and the remaining two to the forms *A* and *B*, respectively, the latter being more populated in clear contradistinction to our results. With dimethyl carbonate the presence of 1–2% of an additional form, probably *B*, was claimed¹⁴ on the basis of temperature dependence of two IR bands whose assignment is questionable^{13,14}. Such a small amount is hardly detectable by another approach and the phenomenon may be also specific for the condensed liquid phase. On the other hand, the claim¹⁵ — based mainly on the carbonyl overtone — that the form *B* prevails in solution of dimethyl carbonate and of other aliphatic carbonates is unsound. Composite carbonyl bands do not prove a conformational equilibrium since they were found even in rigid molecules¹²; in addition, the temperature dependence has never been investigated. Similar reasoning of the same authors³⁰ leads to erroneous conformations even in the case of other esters and were already criticized²⁵. It is true that the conformation of carbonates may be less rigid, *i.e.* the barrier of rotation lower than with other esters. This is suggested by the temperature dependence of dipole moments^{8,9} and of IR spectra¹⁴ as well. Furthermore, methyl *t*-butyl carbonate and similar

* The conformation *A* is, however, at variance with the so-called rabbit-ear effect²⁸. This principle is in our opinion not so generally valid to deserve a particular name.

sterically hindered molecules may behave differently but even in this case the proofs¹⁵ of the conformation *B* are not quite conclusive: Variation of the dipole moment with temperature was followed in a narrow interval only and broadening of the ¹H-NMR signals may have various grounds, compare a different behaviour of tert-butyl formate³¹ existing actually in equilibrium of the *Z*- and *E*-forms.

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REFERENCES

1. Exner O., Jehlička V.: This Journal 35, 1514 (1970).
2. Exner O., Jehlička V., Firl J.: This Journal 37, 466 (1972).
3. Exner O., Plesničar B.: J. Org. Chem. 39, 2812 (1974).
4. Arbuzov B. A., Exner O., Timosheva A. I., Kataev V. E., Vulfson S. G., Vereshchagin A. N.: Izv. Akad. Nauk SSSR, Ser. Khim. 1976, 1246.
5. Exner O., Dembech P., Seconi G., Vivarelli P.: J. Chem. Soc., Perkin Trans. 2 1973, 1870.
6. Exner O. in the book: *The Chemistry of Double-Bonded Functional Groups* (S. Patai, Ed.), p. 1. Wiley-Interscience, London 1977.
7. Sorensen A. M.: Acta Chem. Scand. 25, 169 (1971).
8. Kubo M., Morino Y., Mizushima S.: Sci. Papers Inst. Phas. Chem. Res. (Tokyo) 32, 129 (1937).
9. Yasumi M.: Nippon Kagaku Zasshi 60, 1208 (1939).
10. Arbuzov B. A., Shavsha T. G.: Dokl. Akad. Nauk SSSR 68, 1045 (1949).
11. Longster G. F., Walker E. E.: Trans. Faraday Soc. 49, 228 (1953).
12. Byrne J. S., Jackson P. F., Morgan J. J.: J. Chem. Soc. Perkin Trans. 2 1976, 1800.
13. Collingwood B., Lee H., Wilmschurst J. K.: Aust. J. Chem. 19, 1637 (1966).
14. Katon J. E., Cohen M. D.: Can. J. Chem. 52, 1994 (1974); 53, 1378 (1975).
15. Oki M., Nakanishi H.: Bull. Chem. Soc. Jap. 44, 3419 (1971).
16. Exner O., Jehlička V.: This Journal 30, 639 (1965).
17. Bischoff C. A., Hedenström A. V.: Ber. Deut. Chem. Ges. 35, 3431 (1902).
18. Holleman A. F., Hoeflake J. M. A.: Rec. Trav. Chim. Pays-Bas 36, 272 (1916).
19. Kofler L., Kofler A.: *Thermo-Mikro-Methoden zur Kennzeichnung organischer Stoffe und Stoffgemische*, p. 495. Verlag Chemie, Weinheim 1954.
20. Hoeflake J. M. A.: Rec. Trav. Chim. Pays-Bas 36, 24 (1916).
21. Reverdin F.: Ber. Deut. Chem. Ges. 27, 3458 (1894).
22. Plesničar B., Smolíková J., Jehlička V., Exner O.: This Journal 43, 2754 (1978).
23. Exner O.: *Dipole Moments in Organic Chemistry*, p. 33. Thieme, Stuttgart 1975.
24. Vogel A. I.: J. Chem. Soc. 1948, 1842.
25. Exner O., Bláha K.: This Journal 42, 2379 (1977).
26. Buzek F.: *Thesis*. Prague Institute of Chemical Technology, Prague 1971.
27. Radom L., Lathan W. A., Hehre W. J., Pople J. A.: Aust. J. Chem. 25, 1601 (1972).
28. Eliel E. L.: Accounts Chem. Res. 3, 1 (1970).
29. Exner O., Fidlerová Z., Jehlička V.: This Journal 33, 2019 (1968).
30. Oki M., Nakanishi H.: Bull. Chem. Soc. Jap. 44, 3148, 3197 (1971).
31. Drakenberg T., Forsén S.: J. Phys. Chem. 76, 3582 (1972).