Electric Dipole Moments of Some Heterocyclic Cyclobutane Derivatives in Benzene Solution

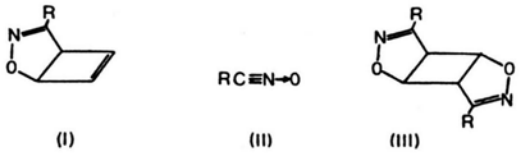
M. Sanesi

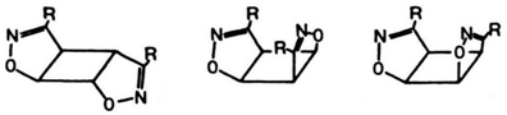
Institute of Physical Chemistry and Electrochemistry, University of Pavia, Pavia, Italy

Z. Naturforsch. **34 a**, 257–259 (1979); received December 18, 1978

The electric dipole moments of some heterocyclic cyclobutane derivatives have been measured in benzene solution at 20 °C. The observed values are compared with those calculated by vector addition for different steric configurations.

1. The cycloaddition reactions of nitrile oxides, diazoalkanes and dienes with the cyclobutene derivative I were recently studied by Bianchi et al. [1]. In particular it was found that in all the reactions investigated the sterically favoured *anti* adducts were formed in larger amounts than the *syn* isomers, and concerning the addition of

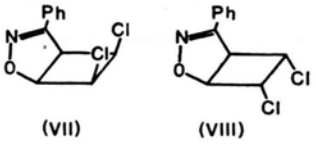




a: R=Me ; b: R=Ph

acetonitrile oxide IIa to Ia, it was considered remarkable that of the four possible isomers IIIa–VIa three only were detected and isolated, i.e., the *anti-trans* IIIa, the *anti-cis* IVa and the *syn-trans* Va. The assignment of these configurations was made on the ground of n.m.r., Raman and i.r. spectra, as well as X-ray structure analysis [2, 3].

Useful additional information may be obtained from the dipole moments of the different adducts, since their values ought to be strongly dependent on the sterical configuration. A brief report is here made of dipole moment measurements carried out on the above tricyclic isomers, as well as on 3-phenyl-Δ^2-isoxazoline and on the *syn* and *anti* adducts VII and VIII, obtained by cycloaddition of benzonitrile oxide IIb to 3.4-*cis*-dichlorocyclobutene [4].



The experimentally observed moments were then compared with the values calculated by vector addition for each steric configuration.

No dipole moment values were previously reported for any of the above compounds.

2. The dilute solution method was employed to evaluate the electric dipole moment, μ, through the usual Debye equation, while the solute orientation polarization at infinite dilution, $P_{2,\mu}$, was obtained from dielectric constant, ε, and refractive index, n, measurements on benzene solutions at 20 °C by means of the Guggenheim [5] extrapolation equation

$$P_{2,\mu} = 3\,M_2(\alpha - 2n_1\gamma)/d_1(\varepsilon_1 + 2)^2 \qquad (1)$$

where α and γ are the slopes of the straight-lines $\varepsilon_{1,2} = \varepsilon_1 + \alpha w_2$ and $n_{1,2} = n_1 + \gamma w_2$, respectively ($w_2$ = solute weight fraction).

The experimental set-up, treatment and characteristics of the solvent, and the evaluation of uncertainties affecting α, γ, $P_{2,\mu}$ and μ as a consequence of data fluctuations, were described elsewhere [6, 7]. For the preparation and purification of the several adducts, reference is made to [1, 4]*, **.

3. The results obtained for all compounds, except adduct IIIa, are summarized in Table 1, where the number of measured solutions and their concentration range (in which the linearity of $\varepsilon_{1,2}$ and $n_{1,2}$ vs. w_2 was verified) are also indicated.

With adduct IIIa, very sparingly soluble in benzene and practically apolar, it was only possible

Reprint requests to Prof. M. Sanesi, Istituto di Chimica Fisica e di Elettrochimica dell'Università, Via Taramelli, 16. I-27100 PAVIA (Italy).

0340-4811 / 79 / 0200-0257 $ 01.00/0

* Thanks are due to Prof. G. Bianchi and R. Gandolfi, Institute of Organic Chemistry, University of Pavia, for having supplied the specimens of the compounds.

** The same references may be consulted for the rational nomenclature of compounds.

Table 1. Slopes of $\varepsilon_{1,2}$ and $n_{1,2}$ vs. w_2, orientation polarizations and dipole moments.

Compound (m.p./°C)	n°. of solns.	concentration range (as $w_2 \cdot 10^3$)	α	γ	$P_{2,\mu}$/cm^3	μ/D
Adduct IVa (146—147)	5	1.73 ÷ 4.04	16.751 ± 0.022	0.0203 ± 0.0037	516.3 ± 0.8	4.98 ± 0.01
Adduct Va (139—140)	7	1.61 ÷ 3.75	10.231 ± 0.044	0.0196 ± 0.0021	314.7 ± 1.4	3.89 ± 0.01
Adduct VII (163)	5	2.30 ÷ 4.80	10.401 ± 0.094	0.0627 ± 0.0017	460.1 ± 4.1	4.71 ± 0.02
Adduct VIII (112—113)	5	2.33 ÷ 4.51	4.188 ± 0.026	0.0674 ± 0.0011	179.5 ± 1.2	2.94 ± 0.01
3-Phenyl-Δ^2-isoxazoline (66—67) (°)	5	4.47 ÷ 17.8	9.033 ± 0.053	0.0795 ± 0.0007	240.9 ± 1.4	3.40 ± 0.01

(°) Prepared according to [8]; recrystallized from ligroine.

to obtain a roughly approximated value, $\mu \approx 0.8$ D, by means of the empyrical Srivastava and Charandas' [9] equation

$$\mu = A\,(M_2\,\alpha)^{1/2} \qquad (2)$$

where A is a constant depending on the solvent (0.9 for benzene at room temperature) and α was derived from a few solutions of very low concentration.

The dipole moment evaluation by vector addition was performed as usual after decomposing the total moment, μ_T, into its components along three properly chosen perpendicular axes. A few simplifying assumptions were introduced, i.e., (i) planar arrangement of the cyclobutane and of the isoxazoline rings, (ii) component moments contributed by the latter equal to the experimental moments of isolated molecules of similar pentaheterocyclic compounds (hereafter indicated as μ_1), and (iii) C–H bond moment (for the hydrogen atoms attached to the cyclobutane ring) equal to zero.

Besides μ_1, the other factors to be considered are: (a) the dihedral angle φ made by one isoxazoline plane and the cyclobutane plane; and (b) the angle β (counted clockwise) between the direction of μ_1 and the line joining the midpoint of the isoxazoline side opposite to the nitrogen atom and the latter atom.

Briefly, the component moments, μ_x, μ_y, and μ_z, can be expressed in terms of the steric configuration and of the partial moments acting within the molecules, and thus be easily calculated as functions of μ_1, φ, and β.

It can be mentioned that on taking into account the X-ray results for adduct IIIa [2], one is led to evaluate on the average $\varphi = 63.5°$; the rounded value of 65° was here taken as the starting point in calculating μ_T in all cases.

Considering first the chlorinated derivatives VII and VIII* the C–Cl bond moment was taken as 1.5 D [10], while μ_1 could be reasonably supposed not to exceed on one side 3.0 D (calculated for 3-phenylisoxazole by Cencioni et al. [11]) and on the other side 3.4 D, as determined in this work for 3-Phenyl-Δ^2-isoxazoline. The angle β was initially taken equal to 33°, as deduced from Ref. [11] data, but the slightly larger value of 40° was also employed. The following results were obtained:

μ_1/D	φ/°	β/°	μ_T/D	
			syn	*anti*
3.4	65	33	5.35	1.85
3.4	65	40	5.27	2.20
3.0	65	33	5.06	1.65
3.0	65	40	4.99	1.99

Should a C–H bond moment of ≈0.4 D, pointing to H, be also taken into account [10, 12], this would result in a decrease of the *syn* moment and an increase of the *anti* one. A substantial, although qualitative, agreement is therefore found between the calculated and observed moments, supporting the assignment of configurations to adducts VII and VIII [4].

On passing to the tricyclic compounds, the value of 65° has been initially retained for angle φ, while for β a value of 28° was derived from Ref. [11] data on 3-methylisoxazole. As for μ_1, considering the observed moments of isoxazole (2.76—2.84 D [13]; 2.90 [14]**), of isoxazoline (2.88 D [15]) and of

* In this case the μ_1 pertinent to one isoxazoline ring is simply substituted with the resultant of two C-Cl bond moments.

** This datum comes from microwave spectroscopic measurements, which also allowed to detect the direction of the molecular dipole: from the latter one obtains $\beta \approx 26°$.

3-methylisoxazole (2.86 D [16], 3.04 D [17]) along with the theoretically calculated one for the latter (2.88 D [11]), there would be no reasons of choosing any value significantly different from 2.9 D.

The symmetrical configuration *anti-trans* would of course give rise to a null dipole moment. Although the observed moment of IIIa (≈ 0.8 D) is to be considered somewhat in excess (mainly because Eq. (2) does not make allowance for atomic polarization)*, it is to be noted that the X-ray analysis [2] proved the cyclobutane ring not to be exactly planar, but slightly puckered, at least in the crystalline state. If such a puckered structure were present also in solution, a definitely non-zero although very small dipole moment would be justified.

Concerning the *syn-trans* configuration, the above set of parameters led to a calculated moment of 4.65 D, to be compared with the observed one in Va (3.89 D). The vector analysis, however, showed that the total moment, μ_T, in this configuration is very sensitive to comparatively small variations of φ and β. Thus, $\mu_T = 3.84$ is obtained with $\varphi = 60°$ and $\beta = 40°$. The observed moment is therefore consistent with the assigned configuration.

Anomalous results were encountered with the *anti-cis* configuration, since the calculated value ($\mu_T = 2.73$ D) is strikingly lower than the observed moment of IVa (4.98 D). Moreover, it can be seen that μ_T is here practically unaffected by large changes in φ: indeed, the extreme values $\varphi = 0°$ and $\varphi = 90°$ would correspond to fictitious configurations, for both of which the resultant moment ($\mu_T = 2\,\mu_1 \sin\beta$) amounts to just 2.72 D. On the other hand, the μ_T for this configuration is markedly affected, although still unsufficiently, by changes in β: when passing from $\beta = 28°$ to $\beta = 45°$, μ_T rises to 4.10 D. A further increase can be achieved only if μ_1 too is substantially increased: thus with $\mu_1 = 3.5$ D and $\beta = 45°$ the result of vector addition ($\mu_T = 4.95$ D) becomes closer to the observed moment. Both parameters, however, appear abnormally high, so that the physical meaning of the large dipole moment found for adduct IVa is at present to be considered as an open question.

* Abnormally high contributions by atomic polarization can be predicted when symmetrical structures with fairly large bond and/or group moments are concerned, as it is the case with IIIa.

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