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DIPOLE MOMENTS OF BORON CHELATES WITH TROPOLONE AND 1,3-DIKETONE DERIVATIVES

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Abstract—Dipole moments were determined for the chelates **2–6** of benzodioxaborole or diphenylborinic acid with tropolone derivatives or with 1,3-diketones (acetylacetone, dibenzoylmethane). Correlations with the structure were attempted.

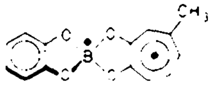
In a previous paper,[1] the dipole moment of the chelate **1** obtained from 2-alkoxy-1,3,2-benzodioxaboroles and β-methyltropolone was measured and found to be 8.24 ± 0.03 D; theoretical estimation of dipole moments from molecules containing parts of structure **1** gave an expected value of 8.6–9.2 D for that structure, while an open non-chelated structure was expected to lead to a value of 4.4–5.7 Debye units.

Taking the chelated structure as firmly established on this basis and through spectroscopic measurements,[2] we now investigated the dipole moments of chelates with the general formulas **2–6** (R = Me or Ph). Compounds **1** and **2** differ only by one Me group.

Table 1. Measurements of dipole moments (in benzene at 30°C)

Comp.	P [cm³]	P_{electr}[a] [cm³]	α $\left(\frac{\partial\epsilon}{\partial c}\right)$	β $\left(\frac{\partial\rho}{\partial c}\right)$	μ [D]
2	1175	71.3	33.5	1.17	7.42 ± 0.1
3	888.5	82.8	25.0	0.50	6.24 ± 0.1
3a	679.8	64.4	18.6	0.75	5.54 ± 0.1
4a	907.7	108.1	24.5	1.26	6.32 ± 0.1
5a[b]	574.7	84.7	15.1	0.70	4.90 ± 0.1
5b	755.5	127.8	19.6	1.32	5.59 ± 0.1
6	1395	74.3	40.8	2.70	8.34 ± 0.4

[a]Sum of atomic refractions.
[b]At 25°C.



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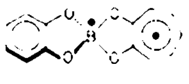

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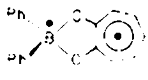

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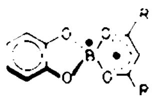

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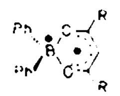

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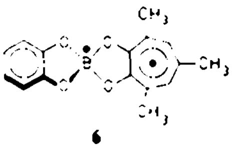

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a, R = Me ; b, R = Ph

EXPERIMENTAL

The synthesis of compounds **2–5** (R = Me and Ph) has been described elsewhere.[3-7] They were purified by recrystallization from benzene. Compound **6** was synthesised from 3,5,7-trimethyltropolone[8] and 2-n-butoxy-1,3,2-benzodioxaborole[2] in benzene, and recrystallised from chloroform–benzene, m.p. 330°.

^{1}H-NMR,[9] IR and UV[10] spectral data for **2–5** were reported earlier. The ^{1}H-NMR spectrum of **6** in deuterochloroform presents the nine Me protons at δ 2.67 (the same accidental degeneracy also occurs in 3,5,7-trimethyltropolone at δ 2.44; the two aromatic protons appear at δ 7.25), the two tropolonic aromatic protons at δ 7.87, the four pyrocatechol protons at δ 6.84 (narrow multiplet).

Dipole moments were measured in benzene, at 30° unless otherwise stated, by determining[11] dielectric permittivities (ϵ) and densities (ρ) for series of 3–5 solns of varying concentrations in the range 0.0005–0.003 molar fractions, excepting **6** which is less soluble and had range 0.00009–0.0002 mole fractions. The strictly linear dependence vs concentration indicates that in this concentration range there is no detectable association.

The results presented in Table 1 were calculated using Hedestrand's equation.[12] Atomic refractions after Eisenlohr were summed to evaluate the electronic polarization P_{electr}. A cor-

Table 2. Dipole moments of compounds 2–5, and in brackets differences between adjacent values (all figures in Debyes)

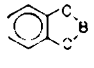
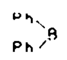
Moieties		(Diff.)		(Diff.)	
	**2** 7.42	(1.10)	**4b** 6.32	(0.78)	**4a** 5.54
(Diff.)	(1.18)		(0.73)		(0.64)
	**3** 6.24	(0.65)	**5b** 5.59	(0.69)	**5a** 4.90

Table 3. CNDO/2 Calculation of dipole moments and of other data for model boron compounds **7** and **8**

			Wiberg bond indices		Dipole	Charges on atoms												
Comp.	(φ)	Energy (Hartree)	1-2	1-16	moment (Debyes)	B	O_2	O_5	O_{16}	C_3	C_4	C_5	C_6	C_7	C_8	C_9	C_{10}	C_{17}
7		−146.6752	0.764	0.912	11.74	0.465	−0.291	−0.291	−0.326	0.213	0.213	†	−0.019	0.084	0	0.084	−0.019	0.005
8	(0°)	−146.4084	1.0678	1.111	6.22	0.484	−0.240	−0.342	−0.242	0.185	0.229	−0.055	0.054	−0.020	0.060	−0.079	†	0.066
8	(30°)	−146.4107	1.055	1.111	6.10	0.487	−0.240	−0.338	−0.247	0.190	0.229	−0.055	0.053	−0.20	0.058	−0.075	†	0.068
8	(60°)	−146.4163	1.023	1.105	6.17	0.489	−0.251	−0.337	−0.252	0.193	0.229	−0.055	0.055	−0.020	0.059	−0.062	†	0.064
8	(90°)	−146.4195	1.010	1.096	6.16	0.490	−0.254	−0.336	−0.257	0.195	0.228	−0.056	0.055	−0.020	0.059	−0.060	†	0.067

†Non-existing atom.

rection was used for calculating atomic polarizations (10% from electronic polarizations).

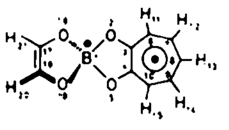
Relative errors of dipole moment determinations are in the range 1–2%, as indicated by two independent measurements for **4a**; however, for **6** the error is about 0.4 D because of the very low solubility.

DISCUSSION OF THE RESULTS

A comparison between the dipole moments of **1** and **2** indicates that introduction of a β-Me group into tropolone increases appreciably (by 0.82 D) the dipole moment of the chelate. This effect is in agreement with the dipole moment of **6**, the highest yet recorded for any boron chelate.

Table 2 presents the dipole moments for chelates **2–6** again, arranged according to the two moieties of the boron chelates. Differences between adjacent dipole moments are indicated in brackets. All these differences are in the range 0.7 ± 0.1 D, with the exception of the two differences for compound **2** which are in the range 1.15 ± 0.1 D. Qualitatively, one may assert that a positive charge is better stabilized by the dibenzoylmethane than by the acetylacetone moiety, and in turn by tropolone than by the dibenzoylmethane moiety. On the other hand, the benzodioxa substituents are more strongly electron-donating than the two phenyl substituents. However, in compound **2**, these two effects are not only added, but a synergistic supplementary effect is manifest. This intramolecular charge transfer of **2** is manifested in the electronic absorption spectrum of **2**, and in a lesser extent, in those of **4a** and **4b**.[10]

A CNDO/2 calculation for model structures **7** and **8** was carried out. Results are presented in Table 3.



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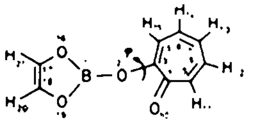

8

It is obvious that for the spiranic structure **7**, Pople's parametrization exaggerates the dipole moment. A non-chelated structure **8** has a minimal calculated dipole moment for a dihedral angle φ of approx. 30° but the variation of the dipole moment with this angle is small: since the calculated dipole moments for a non-chelated structure are too small in all conformations, this is a confirmation that all boron compounds investigated in the present paper have a chelated structure with tetracoordinated B atoms.

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