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PROTON MAGNETIC RESONANCE SPECTRA OF CHELATED BORONIUM AND BERYLLIUM BIS-(1,3-DIKETONATES)

A. Trestianu,* H. Niculescu-Majewska, I. Bally, A. Barabás
and A. T. Balaban*

Institute of Atomic Physics and Institute of Physics, Academy of the R. S. Romania, Bucharest

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Abstract PMR spectra of chelated 2-(β-diketonato)-1,3,2-benzodioxaboroles (I), β-diketonato-diphenylborinates (II), 1,3,2-dioxaborinium salts (III), bis-(β-diketonato)-boronium salts (IV) and beryllium β-diketonates (V) are described and discussed The β-diketones employed were acetylacetone (a), benzoylacetone (b), dibenzoylmethane (c), 3-methylacetylacetone (d) and 3-phenylacetylacetone (e). Peaks due to methyl or methine protons are deshielded additively by phenyl groups, and correlations are made with electronic and geometric factors. The absence of ring current in chelates I, II, IV and V and the similarity of their NMR spectra with those of silicon or metal 1,3-diketone chelates makes it probable that there is no ring current in the latter compounds.

PMR spectra of metallic β-diketone complexes afforded in the last years considerable information about the stereochemistry of the complex and the electronic distribution within the chelate ring. Literature references were recently summarized by Smith and Wilkins.[1] There is, however, still some discussion about the presence[2,3] or absence[4–7] of aromatic delocalization in the 6-membered metal-containing chelate ring, as postulated in 1945 by Calvin.[8]

The chemical shift of the methine proton in the chelate complex is not significantly affected by the nature of the central metallic atom. The usual standard, the methine proton in the *cis*-enol form, was recently criticized, and the enolate anion was proposed instead.[9] The exceptionally low-field methine peak of Si(acac)$_3^{\oplus}$, which had been attributed to benzenoid resonance,[2] is more probably due to the high sensitivity of the methine proton towards electrostatic influences in the chelate molecule.[1]

If the central atom in the chelate complex belongs to the First Row of the Periodic system, then the possibility of benzenoid resonance is ruled out from the outset, since the central atom has sp^3 hybridization and no d-orbitals. This was done by Smith and Wilkins[1] who studied beryllium acetylacetonates (V) and acetylacetoneboron difluorides (VI). Having prepared[10–13] several neutral and ionic boron chelate complexes, we were in possession of a set of compounds with variable electric dissymmetry which might be useful in relationship to the above chelates.

We therefore studied the NMR spectra of five different boron and beryllium chelate compounds with β-diketones:

2-(β-Diketonato)-1,3,2-benzodioxaboroles (I); β-Diketonato-diphenylborinates (II); 1,3,2-Dioxaborinium perchlorates (III); bis-(β-Diketonato)-boronium perchlorates (IV); Beryllium β-diketonates (V).

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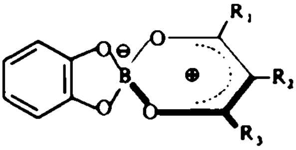
* To whom correspondence should be addressed at P.O. Box 35, Bucharest, Romania.

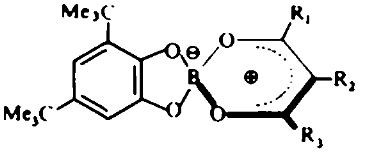
The following β-diketones were employed:

acetylacetone (a): $R_1 = R_3 = Me, R_2 = H$; benzoylacetone (b): $R_1 = Me, R_2 = H, R_3 = Ph$; dibenzoylmethane (c): $R_1 = R_3 = Ph, R_2 = H$; 3-methylacetylacetone (d): $R_1 = R_2 = R_3 = Me$; 3-phenylacetylacetone (e): $R_1 = R_2 = Me, R_3 = Ph$.

The notation of compounds consists in a Roman numeral indicating the boron or beryllium chelate compound, followed by a letter indicating the β-diketone. The numbering indicated in formula VII will be employed.



I



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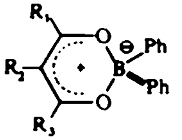

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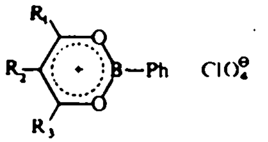

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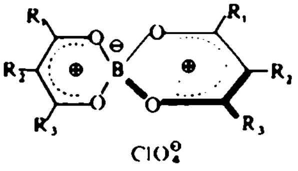

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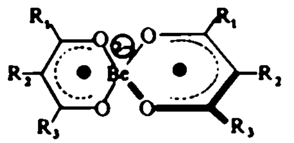
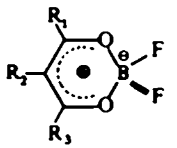


V



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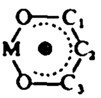


VII

RESULTS AND DISCUSSION

Results are presented in Table 1. The NMR spectra of Ia[10] and of compounds IV[13] were reported earlier, but the relationships between the structure and the chemical shifts were not discussed in detail. The values found for Be(acac)$_2$, Va, agree fairly well with literature data (reported τ values[4,5] for 10% CCl_4 soln 8·02 and 4·53 ppm).

The effect of concentration variations within the range 3–10% is negligibly small on the chemical shifts (less than 0·05 ppm). A change of the solvent from the non-polar carbon tetrachloride to the polar (1·10 D) deuterochloroform or the more polar (1·60 D) sulphur dioxide affects the Me peaks in Ia or Va slightly (less than 0·05 ppm), but the methine peak is shifted to lower fields with increasing polarity of the solvent, as expected, with as much as 0·1–0·2 ppm.

The increasing polarity of the solvent affects the methine peaks of IVa in the opposite way. Since, unlike Ia or Va, IVa is an ionic compound, this effect is probably due to ion-pair association in solvents of lower dielectric constant.

TABLE 1. CHEMICAL SHIFTS RELATIVELY TO INTERNAL TMS (τ VALUES)

Compound		a		b		c	d		e
	Solvent	CH_3	CH	CH_3	CH	CH	1,3-CH_3	2-CH_3	CH_3
I	$CDCl_3$	7·70	4·06	7·58	3·40	2·78			—
	SO_2	7·65	3·85	—	—	—	—	—	
I′	$CDCl_3$	7·68	3·98	7·60	3·32	—	—	—	—
II	$CDCl_3$	7·80	4·40	7·73	3·78	3·06	-	—	-
III	SO_2	—	—	—	-	2·70	—	—	—
IV	$CDCl_3$	7·47	3·36						
	SO_2	7·53	3·54	7·35	2·88	—	7·50	7·88	7·65
V	CCl_4	7·91	4·40	-	—	—	—	—	—
	$CDCl_3$	7·89	4·37	—	—	—	7·85[a]	8·12[a]	—
	SO_2	7·92	4·30	7·75	3·59	2·89			-
VI[a]	$CDCl_3$	7·72	3·96	7·60	3·39	2·82	7·68	8·05	—

[a] Ref. 1.

[b] Other signals not shown in the Table 1, are: Ph groups in Ib, c: τ 1·95–2·60, I′b: τ 1·90–2·40, IIa, b, c: τ 1·85–2·80, IIIc: τ 1·90–3·28, IVb, c, e: τ 1·85–2·50, Vb, c: τ 1·92–2·52; phenylene protons in I and I′: τ 3·15–3·24, t-Bu protons in: I′a: τ 8·57 and 8·68, I′b: τ 8·50 and 8·65.

Methyl peaks. The protons of Me group bonded to C_1 and C_3 resonate at 7·3–8·0 τ. In all cases when both C_1 and C_3 bear a Me substituent, one narrow peak appears indicating equivalence of the two Me groups and the two O atoms.[10, 14] Compound IVd evidences along with the peak due to the six Me protons at C_1 and C_3 a second peak at 7·88 τ due to the three protons of the Me group bonded to C_2. The constant difference between the peaks due to Me bonded to C_2 and the Me groups bonded to C_1 and C_3 (0·38 τ for IVd, 0·37 τ for Vd) is the resultant of the deshielding effect of the oxygens on the Me(C_1, C_3).

The Me chemical shift of acetylacetonates have the following values in deuterochloroform: the neutral beryllium acetylacetonate (Va), 7·89 τ; neutral boron chelate compounds (Ia, IIa and VIa), 7·7–7·8 τ; and bis-diketonato-boronium salts (IVa), 7·47 τ. Though in all these systems the delocalization in the 1,5-oxa-oxoniapentadiene chain is formally identical, electrical influences to the nuclear charge of the central atom, the other substituents attached to it, and the overall charge of the molecule, cause the chelate ring to be electron-richer in the sequence in which the τ value of the Me peaks increases; IVa $<$ VIa $\approx$ Ia $<$ Va $<$ IIa. The same sequence is obtained also for benzoylacetonates (series b).

Substitution of a Me group attached to C_1 or C_3 by Ph causes a downfield shift of the remaining Me, shown in Table 2. The average relative shift is −0·13 τ. This can be explained by the ring-current effect of the Ph group in the plane of the

TABLE 2. RELATIVE Me DOWNFIELD SHIFTS ($\Delta\tau$, PPM) PRODUCED BY Ph SUBSTITUTION

Compounds	I	I'	II	IV	V	VI[1]
Solvent	$CDCl_3$	$CDCl_3$	$CDCl_3$	SO_2	SO_2	$CDCl_3$
b a	0·12	0·08	0·07	0·18	0·17	0·12

molecule. By applying the equation of Pople[15] in a geometry similar to that described in Ref. 1, a theoretical relative shift of $-0{\cdot}12$ τ is calculated, in good agreement with the experiment.

A Ph group bonded to C_2 exerts an upfield shift on the Me groups linked to C_1 and C_3 in IVe, relatively to IVa, of $+0{\cdot}12$ τ. We assign this shift also to a ring current effect, but due to a Ph group which was tilted out of plane by steric interference with the Me groups.

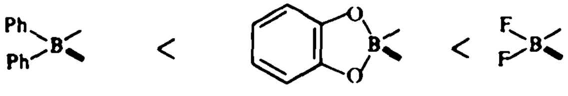
Methine peak. The proton bonded to C_2 resonates over a wide range, 2·7–4·4 τ, according to the solvent and especially to the structural environments.

The methine peak in beryllium β-diketonates V appears at τ values similar to those encountered in a large number of symmetrical neutral metallic β-diketonates.[1,4,5,9] This is an indication that benzenoid resonance (which cannot occur in V) is also absent in these metallic β-diketonates. As a confirmation, the methine peak appearing at 3·36 τ for the cation IVa in $CDCl_3$ is 1·0 ppm downfield from the corresponding peak of the neutral beryllium complex Va, suggesting that the observed[2] low-field resonance in $Si(acac)_3^{\oplus}$ which was interpreted as being due to aromaticity in the chelate is due rather to electrostatic factors.

The chemical shifts of series a, b and c of compounds result in the following sequence of increasing shielding of the methine proton: IV $<$ III $<$ VI $\approx$ I $<$ V $<$ II. This sequence is identical to that observed for the Me peaks; the shift is, however, more important for the methine proton, which is closer to the π-electron cloud.

The most deshielded are the positive ions IV and III, so that one can assert a definite influence of the overall electric charge of the molecule. This is in agreement with literature data.[1,16,17] The symmetrical isoelectronic systems IV and V differ markedly owing to this factor.

The electrically unsymmetrical systems I, II and VI differ owing to the substituents attached to the boron atom. The electron-withdrawing effect of these substituents increases in the sequence:



II I VI

The replacement of a Me by a Ph group causes a pronounced deshielding of the methine proton, just as it deshielded also the Me protons. This downfield shift, presented in Table 3, is remarkably additive in agreement with literature data.[1] For one Ph group the average relative shift is $-0{\cdot}65$ τ. A calculation after Pople affords a close value to the experimental one, indicating that the Ph groups bonded to C_1 and C_3 are coplanar with the chelate ring.

TABLE 3. RELATIVE METHINE DOWNFIELD SHIFTS (Δτ, PPM) PRODUCED BY Ph SUBSTITUTION

Compounds	I	I'	II	IV	V	VI'
Solvent	$CDCl_3$	$CDCl_3$	$CDCl_3$	SO_2	SO_2	$CDCl_3$
b a	0·66	0·66	0·62	0·66	0·71	0·57
c b	0·62	–	0·72	–	0·70	0·57
c a	1·28	-	1·34	-	1·41	1·14

According to this additivity, a peak which appears at τ 2·30 in the NMR spectrum of IVc (cf. footnote b of Table 1) could be ascribed to the methine proton. However, since the NMR spectra of dibenzoylmethane, bis-dibenzoylmethanato-beryllium (Vc), bis-dibenzoylmethanatoboronium perchlorate (IVc) and its methine-deuterated analogue in that region are identical in shape, we must consider this signal as being a part of the Ph multiplet. Therefore the signal of the methine proton could not be detected in IVc, and we assume that it is covered by the Ph multiplet.

Introduction of two t-Bu groups into the phenylene group of I (compounds I') has no effect on the Me signal and produces only a slight (–0·08 ppm) downfield shift of the methine peak, contrary to the expected shift from their inductive effect. This fact proves that there is no long-range transmission of inductive effects in these compounds through the central atom.

EXPERIMENTAL

The syntheses of chelates I,[10] II,[11] III,[12] IV[12, 13] and V[12] were described elsewhere. Dibenzolymethane (c) deuterated in its methylene group was prepared by isotopic exchange in a boiling mixture of dioxan and 99·8% D_2O in the presence of Et_3N. The deuterium content of the methylene group after 3 successive runs was found by analysis to be 78%. Starting from this product compound IVc was obtained in the usual manner. The salt showed a deuterium content calculated for its methine group of 60%. The following solvents were employed for NMR spectra: liquid SO_2, condensed by cooling with a mixture of EtOH and liquid N_2, and dried over $CaCl_2$; CCl_4, distilled over P_2O_5; $CDCl_3$ was a commercial product; TMS was employed as internal standard, and used as a 1% soln in $CDCl_3$ (Silanor-C, Merck, Sharp and Dohme of Canada Ltd.).

The NMR spectra were recorded with a JEOL-3H-60 spectrometer at 60 Mc, and at a temp of 23 ± 2°. The average resolution attained was 0·3 c/s.

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