β-Diketone Boroacetates (Diacetatopropenyleniumdioxyborates)

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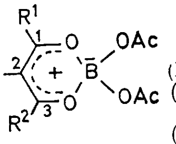
The boroacetate complexes of various β-diketones and β-ketoesters (diacetatopropenyleniumdioxyborates) have been prepared and characterised by their i.r., u.v., and n.m.r. spectra.

THE boroacetate complex of 1-hydroxyanthraquinone has been known for many years,[1] and more recently the borocarboxylates of various enolisable β-diketones have been isolated as intermediates in the preparation of α- and γ-pyrones.[2] Since the field of metal β-diketone chelates has been so active,[3,4] we felt that the preparation and spectroscopic properties of β-diketone boroacetates (diacetatopropenyleniumdioxyborates) should also be investigated. The complexes (I)—(XII) were studied.



	R^1	R^2		R^1	R^2
(I)	Me	Me	(VII)	Bu^t	Bu^t
(II)	Me	Ph	(VIII)	Bu^t	Ph
(III)	Ph	Ph	(IX)	Me	OMe
(IV)	Me	p-$NO_2C_6H_4$	(X)	Me	OEt
(V)	Me	p-BrC_6H_4	(XI)	Ph	OEt
(VI)	Me	p-$MeOC_6H_4$	(XII)	Ph	CF_3

The i.r. spectra show good agreement with previous assignments for similar complexes, while the u.v. absorption maxima and the chemical shift of 2-H can be correlated in most cases with the electronic nature of the substituent groups R^1 and R^2.

EXPERIMENTAL

All starting materials were of the best quality commercially available, with the exception of the β-diketone ligands in (IV)—(VIII), which were prepared by standard methods.[5]

Preparation of Boroacetates.—Boric acid (0·1 mol) was dissolved in acetic anhydride (50 ml) by gently refluxing. The resulting solution of diboron tetra-acetate was cooled and the β-diketone (0·1 mol) was added. The product was recrystallised from acetic anhydride or dry acetone, and stored in vacuum-sealed ampoules to prevent hydrolysis. The complexes were colourless except for (III), (IV), and (VI) which were pale yellow. Attempts to prepare complexes of malonic ester, hexafluoroacetylacetone, and trifluoroacetylacetone were unsuccessful, thus confirming the destabilising effect of the ethoxy and trifluoromethyl groups.[6]

Analyses.—The analytical results and m.p.s. (corrected) are recorded in Table 1. Although data for (VI), (IX), and (XI) were poor, their purity was established by their ^1H n.m.r. spectra and by estimation of the acetic and boric acids liberated on hydrolysis.

TABLE 1

Analytical data

Compound	M.p. (°C)	Yield (%)	Found (%) C	Found (%) H	Found (%) B	Calculated (%) C	Calculated (%) H	Calculated (%) B
(I)	176—178	83	47·3	5·8	4·9	47·4	5·7	4·7
(II)	170—171	76	57·9	5·2	3·7	58·0	5·2	3·7
(III)	223	78	64·8	4·9	3·0	64·8	4·9	3·1
(IV) [a]	185 (decomp.)	71	49·9	4·2	3·0	50·1	4·2	3·2
(V) [b]	158—162	32	45·7	3·8	2·9	45·5	3·8	2·9
(VI)	162—163	42	53·2	5·1	3·8	56·2	5·3	3·4
(VII)	128—129	52	57·7	8·1	3·3	57·7	8·1	3·5
(VIII)	133	65	61·3	6·5	3·1	61·5	6·4	3·2
(IX)	137—138	78	42·7	5·3	4·6	44·3	5·4	4·4
(X)	100—103	30	46·5	6·0	4·1	46·5	5·9	4·2
(XI)	90	22	52·3	5·5	3·4	56·4	5·4	3·4
(XII) [c]	157—162	85	48·5	3·3	3·1	48·8	3·5	3·2

[a] Found: N, 4·3. Calc: N, 4·2%. [b] Found: Br, 21·6. Calc.: Br, 21·6%. [c] Found: F, 16·6. Calc.: F, 16·6%.

Spectra.—I.r. spectra were recorded on Perkin-Elmer 137 and 457 instruments, using Nujol and Florube No. 2 mulls. U.v. spectra were measured on a Perkin-Elmer 137 u.v. spectrometer in methylene dichloride solutions. ^1H N.m.r. spectra were recorded on a Varian HA-100D instrument at the Physico-chemical Measurement Unit, Harwell, using 10% solutions in deuteriochloroform at ambient temperature, with tetramethylsilane as internal reference.

RESULTS AND DISCUSSION

I.r. Spectra.—Some of the most intense bands are common to the whole series, and are assigned as shown in Table 2. These assignments are based on those for

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comparable boron and beryllium chelates,[7-9] and on our own comparisons with the spectra of the free diketones. The bands are generally broadened by chelation and isotopic effects, and interpretation is made difficult by close overlap in several regions. The two closely spaced bands between 1490 and 1600 cm^{-1} have caused much confusion in the literature,[8-11] and we have chosen the definitive assignments of Junge and Musso,[9] who used isotopic labelling to identify each band in the spectra of various metal derivatives. It has, however, been emphasised [12] that such assignments are only approximate, because the vibrations must be extensively coupled.

TABLE 2

I.r. frequencies (cm^{-1})

Range	Assignment
1700—1725	C=O (Acetate groups)
1540—1600 sym	$C\cdots O$ (Chelated)
1490—1570 asym	$C\cdots C\cdots C$
1365—1385 asym	$\left\{\begin{matrix}C\cdots O\\ B{-}O\end{matrix}\right\}$ Overlapping
1260—1280	C—O (Acetate groups)
1040—1075 sym	B—O

U.v. Spectra.—The most intense bands are summarised in Table 3. Weaker bands were also observed for the phenyl derivatives in the region 250—290 nm, which is characteristic of the benzene ring. The former bands correspond very closely to the strongest bands for boron difluoride complexes,[11] and may be attributed to charge-transfer transitions in the delocalised π electron system of the chelating ligands. The $\Delta\lambda$ values show the wavelength shift relative to compound (I); they are approximately additive for the phenyl group (*ca.* +40 nm) in (II), (III), (VIII), and (XI), and for the alkoxy-group (*ca.* −24 nm) in (IX)—(XI). This type of additivity has been noted [13] in the u.v. spectra of the free ligands. The phenyl group is bathochromic because it extends the conjugated system by electron release.[10,13] This effect is reinforced by $+M$ *para*-substituents, particularly the methoxy-group, where the excited state is stabilised by a strong contribution from a *p*-quinonoid structure. However, when an alkoxy-group is substituted *directly* on the chelate ring, it gives a marked hypsochromic effect [compounds (IX)—(XI)]. In the present state of theory, it is impossible to explain these opposing effects in a consistent manner.

TABLE 3

U.v. and n.m.r. data

Compound	$\lambda_{max.}$/nm (± 1)	$\Delta\lambda$/nm	log ε	δ(2-H) ($\pm 0{\cdot}02$)	$\Delta\delta$
(I)	295	0	4·25	6·02	0
(II)	335	+40	4·30	6·64	+0·62
(III)	370	+75	4·57	7·27	+1·25
(IV)	330	+35	4·22	6·72	+0·70
(V)	340	+45	4·96	6·61	+0·59
(VI)	363	+68	4·68	6·54	+0·52
(VII)	296	+1	4·20	6·20	+0·18
(VIII)	337	+42	4·39	6·73	+0·71
(IX)	270	−25	4·47	5·49	−0·53
(X)	272	−23	4·19	5·47	−0·55
(XI)	312	+17	4·31	6·09	+0·07
(XII)	332	+37	4·61	7·08	+1·06

N.m.r. Spectra.—In compound (I) the methyl groups were equivalent, which confirms the cyclic nature of these complexes. Here we report only the chemical shifts for 2-H, which are given in Table 3. The last column gives the change in chemical shift relative to compound (I); positive values of this increment indicate a deshielding effect. As in the case of the u.v. spectra, additivity is observed for the phenyl (+0·62 p.p.m.) and alkoxy-groups (−0·55 p.p.m.), and also for the t-butyl group (+0·09 p.p.m.). These increments are obtained by comparing the $\Delta\delta$ values for compounds (II), (III), and (VII)—(XI). Very similar additivity effects have also been reported for other β-diketone complexes.[10,14,15]

The deshielding effect of the phenyl group may be attributed to ring-current anisotropy.[15] *X*-Ray studies [16] have shown that dibenzoylmethane and its copper(II) complex are completely planar. Assuming that this coplanarity also exists in solution, Trestianu and his co-workers [14] have used the Pople method to calculate the magnitude of this shift, and obtained a value which agrees well with our result and the average shift (0·65 p.p.m.) for their own boron and beryllium complexes. Slight variations in the observed shifts may be correlated with the polarity of the complex.[15] The n.m.r. pattern for the unsubstituted phenyl group itself is very complex at 100 MHz, implying an AA′BB′C system. A previous report,[13] based on an A_3BC interpretation, is in error, because the spectrum is deceptively simple at 60 MHz.

Unlike the phenyl group, it is not possible to quantify the effects of the other substituents R^1 and R^2 on 2-H. However, they are all qualitatively consistent with the electron-attracting or -releasing properties of these groups. In particular, and in contrast to its varied effect on electronic transitions, the methoxy-group shows a consistently shielding effect, both in the *para*-position on a phenyl group and when directly attached to the chelate ring. This is most simply ascribed to the $+M$ effect, which in both cases would increase the electron density on C-2 and shield the adjoining proton. Hammel and Smith [15] reported a similar shielding effect by the *para*-methoxy-group in benzoylacetone and its complexes with BF$_2$, Si, and Al. They interpreted this on the basis of their ' through-space ' dipole field theory,

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but unfortunately their arguments appear inconsistent. Thus, they assume that the polarity of the methoxy-group *opposes* the induced moment in the benzene ring, so that for polar complexes, $\Delta\delta$ is reduced. At the same time they argue that the polarisation of the phenyl group itself reduces $\Delta\delta$ as the polarity of the complex increases. The dipole field theory has been criticised by other authors,[17] and it appears that the effect of molecular polarity might equally well be explained by a ' through-bond ' inductive effect.

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