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# β-DIKETONE INTERACTIONS
## Part 9. The X-ray crystal structure of 2,2-difluoro-4,6-dimethyl-5-(4′-nitrophenyl)-1,3,2-dioxaborinane ($C_{11}H_{10}BF_2NO_4$)*

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## ABSTRACT

2,2-Difluoro-4,6-dimethyl-5-(4′-nitrophenyl)-1,3,2-dioxaborinane shows an unusual degree of hydrolytic stability. An X-ray crystal structure determination reveals a nearly planar 1,3,2-dioxaborinane ring. The bond length and dihedral angle to the phenyl ring show that delocalization of the formal positive charge is confined to the heterocyclic ring.

## INTRODUCTION

The ability of β-diketones to form so-called $BF_2$ chelates (**I**) has been known for many years, primarily because they are intermediates in the formation of β-diketone [2–8]. These compounds have a bonding situation the opposite to that of the alkaneboronic esters (**II**). In these latter compounds the ring is expected to be planar at the boron centre but otherwise to adopt a chair configuration [9]. In (**I**) however the whole ring could be planar even though the boron is tetrahedral. The effect of this configuration at boron on the rest of the ring is unknown. In addition the ring is formally a zwitterion, with the negative charge centred on the boron and the positive charge centred on the middle carbon, although in practice this would be delocalized over neighbouring atoms including the exocyclic group attached to this carbon.

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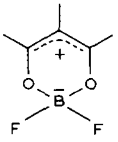
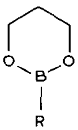


(I)



(II)

$BF_2$ chelates have also been made and used in the study of the $^{13}C$ NMR spectra of the enol tautomers of β-diketones [10, 11]. In this work $BF_2$ derivatives of pentane-2,4-dione and benzoylacetone were compared with the "proton chelates", i.e. the enol tautomers. Since the $^{13}C$ NMR spectra of the $BF_2$ derivatives and the enol tautomers were very similar it was implied that the ring bonding was also similar, i.e. symmetrical. This was taken to include the hydrogen bond itself. This conclusion is now known to be wrong [12].

To the best of our knowledge no crystal structure determination of a compound ring (**I**) has been reported. In our recent studies [13–15] of the effect of substitution at the alpha position of β-diketones on the hydrogen bonding of the enol tautomer we obtained crystals of the title compound as an intermediate in the synthesis of 3-(4′-nitrophenyl)-pentane-2,4-dione. The intermediate was surprisingly stable to hydrolysis and survived even steam distillation. In the preparation of β-diketones by the $BF_3$ method, the final hydrolysis step to remove the $BF_2$ is easily achieved. This unexpected stability prompted us to look more closely at this intermediate in the hope of finding some bonding feature that could explain the observation, such as delocalization between the heterocyclic and phenyl rings. This in turn would be relevant to our researches on the strong hydrogen bonding of 3-substituted-pentane-2,4-diones [1,13–15].

## EXPERIMENTAL

### *2,2-Difluoro-4,6-dimethyl-5-(4′-nitrophenyl)-1,3,2-dioxaborinane* ($C_{11}H_{10}BF_2NO_4$)

This compound was obtained as an intermediate in the synthesis of 3-(4′-nitrophenyl)-pentane-2,4-dione. This β-diketone was to be prepared by the $BF_3$ method from 4′-nitrophenylpropan-2-one and acetic anhydride [4]. $BF_3$ gas was passed into an ice-cooled mixture of 4′-nitrophenylpropan-2-one (1.79 g, 10 mmol) and acetic anhydride (1.10 g, 10.1 mmol) for 2.75 h, at the end of which time the reaction mixture was a solid mass. This was steam distilled and the distillate separated into an oil, aqueous layer and crystals when left overnight. The solid product was recrystallized from petroleum ether (40–60) to give a 41% yield of 2,2-difluoro-4,6-dimethyl-5-(4′-nitrophenyl)-1,3,2,-dioxaborinane, m.p. 38 °C.

### *Crystallography*

$C_{11}H_{10}BF_2NO_4$, $M=269.01$, monoclinic, space group $P2_1/a$, $a=12.027(3)$, $b=13.986(1)$, $c=7.189(2)$ Å, $\beta=90.58(2)^\circ$, $U=1209.1(5)$ Å$^3$, $z=4$, $D_c=1.478$ g cm$^{-3}$, $F(000)=552$, $\lambda=0.71069$ Å, $\mu$(Mo $K\alpha$)$=1.2$ cm$^{-1}$, crystal dimensions $0.73\times0.20\times0.20$ mm.

### *Data collection*

Unit cell parameters and intensity data were attained by following previously detailed procedures [17], using a CAD-4 diffractometer operating the $\omega$-$2\theta$ scan mode, with graphite monochromated Mo $K\alpha$ radiation. A total of 2124 unique reflections were collected ($3<2\theta<50^\circ$). The segments of reciprocal space scanned was ($h$) $-14\rightarrow14$, ($k$) $0\rightarrow16$, ($l$) $0\rightarrow8$.

### *Structure solution and refinement*

The structure was solved by routine direct methods (SHELX-86 [18]), and refined by full-matrix least squares (SHELX-76 [19]). All non-hydrogen atoms were refined anisotropically. Methyl and phenyl hydrogen atoms were placed into calculated positions (C–H 0.96 Å, $U=0.10$ Å$^2$). All calculations were performed on a DEC VAX-11/750 computer.

TABLE 1

Fractional atomic coordinates ($\times10^4$) for 2,2-difluoro-4,6-dimethyl-5-(4′-nitrophenyl)-1,3,2-dioxaborinane, $C_{11}H_{10}BF_2NO_4$

| | $x$ | $y$ | $z$ |
|---|---|---|---|
| O(1) | 3990(2) | 4674(1) | 7680(3) |
| O(2) | 3219(2) | 4127(1) | 10586(3) |
| O(3) | 4558(2) | −1403(2) | 6848(4) |
| O(4) | 3143(2) | −1175(2) | 5054(4) |
| B | 3326(3) | 4949(2) | 9319(6) |
| F(1) | 3836(2) | 5681(1) | 10209(3) |
| F(2) | 2288(2) | 5206(1) | 8710(3) |
| N | 3861(2) | −884(2) | 6128(4) |
| C(1) | 4742(3) | 3651(2) | 5422(6) |
| C(2) | 4125(2) | 3790(2) | 7193(5) |
| C(3) | 3754(2) | 3043(2) | 8282(4) |
| C(4) | 3338(3) | 3254(2) | 10019(5) |
| C(5) | 3000(4) | 2510(2) | 11346(5) |
| C(6) | 3837(2) | 2024(2) | 7649(4) |
| C(7) | 3015(2) | 1652(2) | 6468(4) |
| C(8) | 3022(3) | 710(2) | 5943(4) |
| C(9) | 3867(2) | 134(2) | 6615(4) |
| C(10) | 4717(3) | 481(2) | 7736(4) |
| C(11) | 4696(3) | 1432(2) | 8233(4) |

TABLE 2

Bond lengths (Å) and bond angles (°) for 2,2-difluoro-4,6-dimethyl-5-(4′-nitrophenyl)-1,3,2-dioxaborinane, $C_{11}H_{10}BF_2NO_4$

| Parameter | Value | Parameter | Value |
|---|---|---|---|
| *Bond lengths* | | | |
| B-O(1) | 1.481(5) | C(2)-O(1) | 1.296(4) |
| B-O(2) | 1.473(5) | C(4)-O(2) | 1.296(4) |
| N-O(3) | 1.220(4) | N-O(4) | 1.223(4) |
| F(1)-B | 1.352(5) | F(2)-B | 1.367(5) |
| C(9)-N | 1.466(4) | C(2)-C(1) | 1.492(5) |
| C(3)-C(2) | 1.382(5) | C(4)-C(3) | 1.382(5) |
| C(6)-C(3) | 1.499(5) | C(5)-C(4) | 1.471(5) |
| C(7)-C(6) | 1.397(5) | C(11)-C(6) | 1.387(5) |
| C(8)-C(7) | 1.371(5) | C(9)-C(8) | 1.380(5) |
| C(10)-C(9) | 1.383(5) | C(11)-C(10) | 1.377(5) |
| *Bond angles* | | | |
| C(2)-O(1)-B | 122.1(3) | C(4)-O(2)-B | 122.0(4) |
| O(2)-B-O(1) | 110.0(3) | F(1)-B-O(1) | 109.1(4) |
| F(1)-B-O(2) | 109.9(4) | F(2)-B-O(1) | 108.2(4) |
| F(2)-B-O(2) | 108.6(4) | F(2)-B-F(1) | 111.1(4) |
| O(4)-N-O(3) | 123.2(4) | C(9)-N-O(3) | 118.3(4) |
| C(9)-N-O(4) | 118.5(3) | C(1)-C(2)-O(1) | 114.7(4) |
| C(3)-C(2)-O(1) | 121.7(4) | C(3)-C(2)-C(1) | 123.5(4) |
| C(4)-C(3)-C(2) | 118.2(4) | C(6)-C(3)-C(2) | 121.6(4) |
| C(6)-C(3)-C(4) | 120.2(3) | C(3)-C(4)-O(2) | 121.9(4) |
| C(5)-C(4)-O(2) | 115.5(4) | C(5)-C(4)-C(3) | 122.7(4) |
| C(7)-C(6)-C(3) | 119.3(3) | C(11)-C(6)-C(3) | 121.8(3) |
| C(11)-C(6)-C(7) | 118.8(3) | C(8)-C(7)-C(6) | 121.3(3) |
| C(9)-C(8)-C(7) | 118.1(4) | C(8)-C(9)-N | 118.7(3) |
| C(10)-C(9)-N | 118.8(3) | C(10)-C(9)-C(8) | 122.5(3) |
| C(11)-C(10)-C(9) | 118.4(4) | C(10)-C(11)-C(6) | 120.9(4) |

The final residuals $R$ and $R_w$ were 0.049 and 0.052 respectively for the 178 variables and 1399 data for which $F_0 > 6\sigma(F_0)$. The function minimized was $\Sigma_w(|F_0| - |F_c|)^2$ with the weight being defined as $1/[\sigma^2(F_0) + 0.00008F_0^2]$.

Atom co-ordinates are given in Table 1, and bond lengths and angles in Table 2. The structure and atom labelling are shown in Figs. 1 and 2. Non-hydrogen atom anisotropic temperature factors, hydrogen fractional atomic co-ordinates and isotropic temperature factors, and selected non-bonded distances are available as supplementary data*.

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*B.L.L.D. Supplementary Publication number S.U.P. 26368 (17 pages).

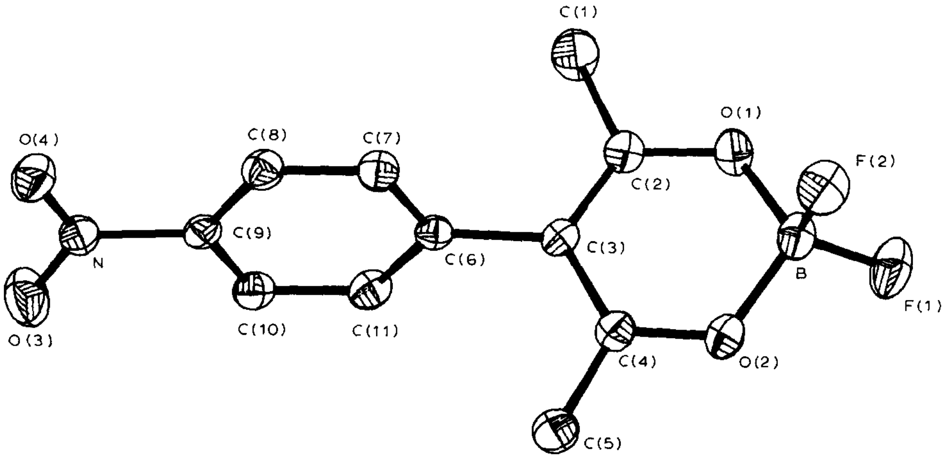

Fig. 1. Diagram of 2,2-Difluoro-4,6-dimethyl-5-(4′-nitrophenyl)-1,3,2-dioxaborinane showing atom labelling scheme.

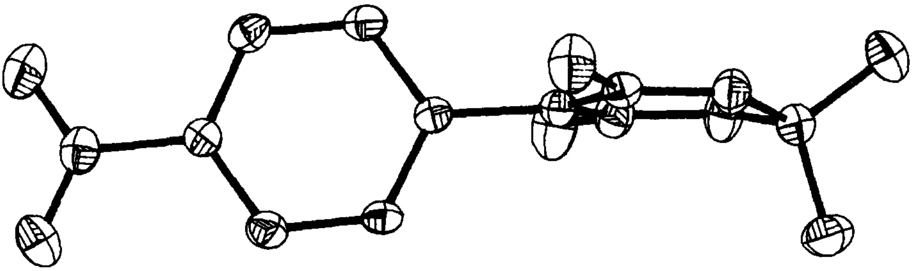

Fig. 2. Diagram of 2,2-Difluoro-4,6-dimethyl-5-(4′-nitrophenyl)-1,3,2-dioxaborinane showing end-on view of heterocyclic ring.

## DISCUSSION

The heterocyclic compound, 2,2-difluoro-4,6-dimethyl-5-(4′-nitrophenyl)-1,3,2-dioxaborinane, is surprisingly stable to hydrolysis. 1,3,2-Dioxaborinanes are intermediates in the synthesis of $\beta$-diketones by the $BF_3$ method [5]. This ring succumbs to hydrolysis to release the $\beta$-diketone. However in the reaction to prepare 3-(4′-nitrophenyl)-pentane-2,4-dione, the title compound resisted hydrolysis and was evolved during steam distillation of the reactants. It crystallized overnight from the heterogeneous mixture from the steam condensate. (The desired product was obtained by an alternative method and its structure has recently been reported [1]).

The structure of the 1,3,2-dioxaborinane ring is perfectly symmetrical with a tetrahedrally coordinated boron. The locus of the corresponding positive charge of the zwitterion should be on C3. As expected the ring shows extensive delocalization. Curiously the bond lengths O1–C2 (1.296(4) Å), C3–C4 (1.382(5) Å) and O1–O2 (2.419 Å) are very like those of the enol half of 3-(4′-nitrophenyl)-pentane-2,4-dione, which are 1.309, 1.379 and 2.445 Å respectively [15]. The bonds of the carbonyl half of the enol ring are C–O = 1.270(4) Å and C–C = 1.499(4) Å.

The differences between the two sides of the enol ring are not large and this explains the NMR observations of Shapet'ko et al. [10, 11]. It is somewhat surprising that there is such a small difference in chemical shift and bond lengths between the two compounds, considering the title compound carries a formal charge separation over the heterocyclic ring (**I**). The bond lengths imply very little charge separation; rather there is a delocalized $\pi$-system extending over all ring atoms except boron.

Further support for this comes from the configuration of the two rings. Had the positive charge of (**I**) been localized only over the carbon atoms of the ring (C2, C3 and C4) then it might also have been partly delocalized over the phenyl ring with its component nitro group. However this does not occur. The C3–C6 bond length is that of a single bond and the two rings are orientated with a dihedral angle between them of 99°, which would prevent any overlap between the $\pi$ orbitals on C3 and C6. As Fig. 2 shows, the 1,3,2-dioxaborinane ring is almost planar, with the boron atom ca. 0.2 Å below the plane.

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## REFERENCES

1 Part 8: J. Emsley, L.Y.Y. Ma, P. Bates and M.B. Hursthouse, J.. Chem. Soc., Perkin Trans, 1, (1989) 5.

2 F.G. Young, F.C. Frostick, J.J. Sanderson and C.R. Hauser, J. Am. Chem. Soc., 72 (1950) 3231.

3 C.R. Hauser, F.C. Frostick and E.H. Man, J. Am.. Chem. Soc., 74 (1952) 3231.

4 C.R. Hauser and C.J. Eby, J. Am.. Chem. Soc., 79 (1957) 725.

5 R.M. Manyik, F.C. Frostick Jr., J.J. Sanderson and C.R. Hauser, J. Am. Chem. Soc., 75 (1953) 5030.

6 H. Musso and K. Figge, Justus Liebigs Ann. Chem., 668 (1963) 1.

7 A.N. Sagredos, Justus Liebigs Ann. Chem., 700 (1966) 29.

8 J.P. Tuchagues, P. Castan, C. Commenges and J.P. Laurent, Syn. React. Inorg. Metal-Org. Chem., 5 (1975) 279.

9 F.A. Davis, I.J. Turchi, B.E. Maryanoff and R.O. Hutchins, J. Org. Chem., 37 (1972) 1583.

10 N.N. Shapet'ko, S.S. Berestov, V.G. Medvedeva, A.P. Skoldinov and Y.S. Andreichikov, Dokl. Akad. Nauk SSSR, 234 (1977) 566; 234 (1977) 876 (English translation).

11 N.N. Shapet'ko, S.S. Berestova, D.N. Shigorin, V.G. Medvedeva, A.P. Skoldinov, G.D. Plakhina and Y.S. Andreichikov, Theor. Exp. Khim., 15 (1979) 449; 15 (1979) 575 (English translation).

12 J. Emsley, Struct. Bonding, 57 (1984) 147.
13 J. Emsley, N.J. Freeman, P.A. Bates and M.B. Hursthouse, J. Chem. Soc., Perkin Trans. 1, (1988) 297.
14 J. Emsley, L.Y.Y. Ma, P.A. Bates and M.B. Hursthouse, J., Mol. Struct., 178 (1988) 297.
15 J. Emsley and N.J. Freeman, J. Mol. Struct., 161 (1987) 193.
16 A.C.T. North, D.C. Phillips and F.S. Mathews, Acta Crystallogr., Sect. A, 24 (1986) 351.
17 M.B. Hursthouse, R.A. Jones, K.M.A. Malik and G. Wilkinson, J. Am.. Chem. Soc., 101 (1979) 4128.
18 G.M. Sheldrick, SHELX-76 Program for Crystal Structure Determination and Refinement, University of Cambridge, 1976.
19 G.M. Sheldrick, SHELX-86 Program for Crystal Structure Solution, University of Gottingen, 1986.