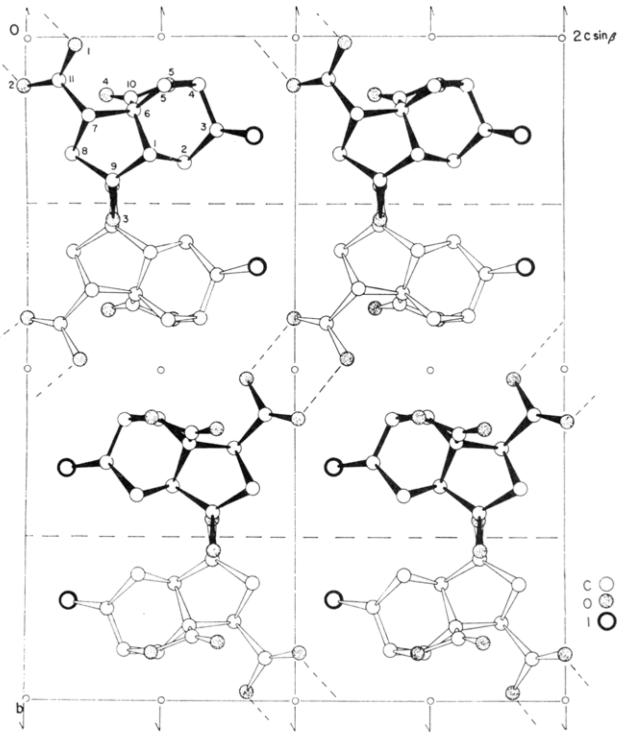

Figure 1.—View of the molecular packing down the *a* axis.

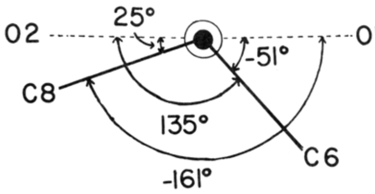

Figure 2.—The torsion angles around the C(7)–C(11) bond. The angle ABCD is considered positive, if, when looking from B to C, atom A has to be rotated clockwise to eclipse atom D.

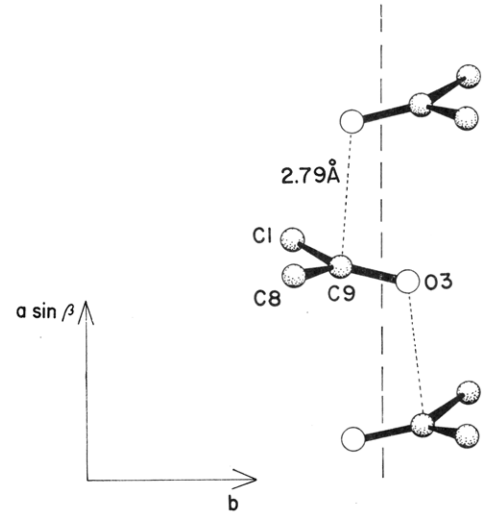

Figure 3.—The arrangement of carbonyl groups looking along the *z* direction.

The torsion angles involving the carboxyl group are shown in Figure 2. Both the C–O bond lengths [C(11)–O(2), 1.20 (4); C(11)–O(1), 1.34 (4) Å] and the torsion angles around the C–C (carboxyl) bond, according to Dunitz and Strickler,[10] suggest that C(11)–O(2) is the double bond in the carboxyl group. The O(1)···O(2) distance involved in an intermolecular hydrogen bond is 2.63 (3) Å. Of particular note is the C(9)···O(3) $(^1/_2 + x, {}^1/_2 - y, z)$ contact of 2.79 (5) Å (Figure 3). This rather short distance between a carbon atom of a carbonyl group and the oxygen atoms of a symmetry-related carbonyl group is similar in length to those observed in chloranil[11] and in alloxan,[12,13] although the geometric disposition of groups resembles rather that found in perdeuterated violuric acid monohydrate.[14] There may also be a C–H···O hydrogen bond (length 3.23 Å) between C(7) and O(4) (at $1 + x, y, z$) although the existence of such interactions is still a matter of lively debate.[15,16]

Registry No.—**4,** 28128-99-6.

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[10] J. D. Dunitz and P. Strickler, "Structural Chemistry and Molecular Biology," A. Rich and N. Davidson, Ed., W. H. Freeman, San Francisco, Calif., 1968, pp 595–602.

[11] S. S. C. Chu, G. A. Jeffrey, and T. Sakurai, *Acta Crystallogr.*, **15**, 661 (1962).

[12] W. Bolton, *ibid.*, **17**, 147 (1964).

[13] C. K. Prout and S. C. Wallwork, *ibid.*, **21**, 449 (1966).

[14] B. M. Craven and Y. Mascarenhas, *ibid.*, **17**, 407 (1964).

[15] J. Donohue in ref 10, pp 443–465.

[16] W. C. Hamilton and J. A. Ibers, "Hydrogen Bonding in Solids," W. A. Benjamin, New York, N. Y., 1968, pp 182–183.

The Effect of Alkyl Substitution on the Boron-11 Chemical Shifts in Aminoboranes and Borates[1a]

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There is considerable evidence[2] that ^{11}B chemical shifts are controlled by the degree of electron occupancy of the vacant p_z orbital on boron. Thus, compounds containing trivalent boron absorb at much lower field than do quadrivalent boron complexes, and the shift to low field is greatest for compounds in which trivalent boron is attached to groups lacking p or π electrons. Trimethylborane, for example, has the lowest known chemical shift (-86.4 ppm[3]) relative to boron trifluoride etherate (EBT),[4] while compounds with groups capable of donating electrons to boron appear at much higher field (*e.g.*, -18.1 ppm for trimethyl borate).[3]

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[1] (a) Reported in part at the 159th National Meeting of the American Chemical Society, Houston, Texas, Feb 1970; (b) National Science Foundation Undergraduate Research Participant, 1969.

[2] (a) G. R. Eaton, *J. Chem. Educ.*, **46**, 547 (1969); (b) J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Vol. II, Pergamon Press, New York, N. Y., 1968, p 970; (c) P. C. Lautherbur in "Determination of Organic Structure by Physical Methods," Vol. II, F. C. Nachod and W. D. Phillips, Ed., Academic Press, New York, N. Y., 1962, p 476.

[3] W. D. Phillips, H. C. Miller, and E. L. Muetterties, *J. Amer. Chem. Soc.*, **81**, 4496 (1959).

[4] All chemical shifts reported in this paper are relative to EBT.

If this was the only factor involved, one would expect the chemical shift of boron to depend on the π-donating ability of the attached group. In fact, one would expect a dimethylamino group to be more effective than a methoxy group. However, for aliphatic boron compounds the reverse appears to be true; thus, tris(dimethylamino)borane absorbs at much lower field (−27.2 ppm[5]) than does trimethyl borate. Until this and other anomalies are resolved, the quantitative prediction of ^{11}B chemical shifts will be impossible.

The more effective shielding of boron by an alkoxy group than by an alkylamino group may be explained in at least two ways. The presence of additional pairs of unshared electrons on atoms adjacent to boron, over and above those needed for π bonding, may increase the shielding on boron.[6] Alternatively, steric repulsion between the alkyl groups may decrease the shielding of boron.

In order to obtain information about the effect on nonbonding interactions on the ^{11}B chemical shift, we have prepared a series of alkylaminoboranes (I–III) and alkyl borates (IV) and measured their boron chemical shifts. These results are summarized in Table I.

$(RNH)_3B$
Ia, R = methyl
b, R = ethyl
c, R = *n*-propyl
d, R = isopropyl
e, R = *sec*-butyl
f, R = *tert*-butyl

$(R_2N)_2BCl$
IIIa, R = methyl
b, R = ethyl
c, R = isopropyl

$(R_2N)_3B$
IIa, R = methyl
b, R = ethyl
c, R = *n*-propyl
d, R = isopropyl

$(RO)_3B$
IVa, R = *n*-butyl
b, R = isobutyl
c, R = *sec*-butyl
d, R = *tert*-butyl
e, R = *n*-pentyl
f, R = isopentyl
g, R = neopentyl

TABLE I

^{11}B CHEMICAL SHIFTS FOR COMPOUNDS I–IV

Compd	Ref	Solvent	Chemical shift[a]	Line width,[b] Hz
Ia	*c*		−24.6[d]	
Ib	*c*	Neat	−23.6	91
		Benzene	−23.3	68
Ic	*e*	Neat	−23.7	174
		Benzene	−23.3	91
Id	*c*	Neat	−22.5	134
		Benzene	−22.4	96
Ie	*c*	Neat	−22.9	215
		Benzene	−22.6	116
If	*c*	Neat	−22.8	185
		Benzene	−22.7	91
IIa			−27.2[f]	
IIb			−28.7[d]	
IIc	*g*	Benzene	−29.2	307
IId	*h*	Benzene	−28.4	495
IIIa	*i*		−27.9[d]	
IIIb	*i*		−28.4[d]	
IIIc	*h*	Neat	−30.6	262
IVa	*j*	Neat	−18.0	141
IVb	*j*	Neat	−17.9	155
IVc	*j*	Neat	−17.7	118
IVd	*j*	Neat	−15.6 (−15.5)[d]	92
		Acetonitrile	−15.8	110
IVe	*k*	Neat	−17.7	237
IVf	*l*	Neat	−17.7	253
		Carbon disulfide	−18.0	108
IVg	*j*	Carbon disulfide	−17.9	123

[a] In parts per million relative to boron trifluoride etherate. Estimated error ±0.15 ppm for line widths >100 Hz, ±0.3 ppm for line widths >200 Hz, ±1 ppm for wider lines. [b] At half-height; estimated error ±5%. [c] D. W. Aubrey and M. F. Lappert, *J. Chem. Soc.*, 2927 (1959). [d] H. North and H. Vahrenkamp, *Ber.*, **99**, 1049 (1966). [e] M. F. Lappert and H. Pyszora, *J. Chem. Soc.*, 1744 (1963). [f] Reference 5. [g] D. W. Aubrey, W. Gerrard, and E. F. Mooney, *J. Chem. Soc.*, 1786 (1962). [h] M. F. Lappert and M. K. Majumdar, *J. Organometal. Chem.*, **6**, 316 (1966). [i] W. Gerrard, M. F. Lappert, and C. A. Pearce, *J. Chem. Soc.*, 381 (1957). [j] W. Gerrard and M. F. Lappert, *ibid.*, 2545 (1951). [k] W. Gerrard and M. F. Lappert, *Chem. Ind. (London)*, 53 (1952). [l] C. R. Kinney, H. T. Thompson, and L. C. Cheney, *J. Amer. Chem. Soc.*, **57**, 2396 (1935).

The chemical shifts of the compounds listed in Table I were independent of solvent and the line widths narrowed on dilution. This is apparently due to lowering of the viscosity of the sample.[7]

The most favorable conformation for an adjacent group containing p electrons to shield boron will be when the unshared pair of electrons and the p_z orbital on boron are coplanar. If nonbonded interactions reduce this coplanarity, shielding of boron will be decreased. Oxygen may therefore be able to shield boron better than nitrogen because the borates have fewer nonbonded interactions than the aminoboranes. An unshared pair of electrons has fewer nonbonded repulsive interactions than an alkyl group.[8]

This hypothesis is supported by the results in Table I. The alkyl borates (series IV) are shielded compared to the monoalkylaminoboranes (series I) which are shielded compared to the dialkylaminoboranes (series II). The molecular structure of trisdimethylaminoborane (IIa)[9] further supports this interpretation. The structure indicates that the dimethylamino groups are twisted out of the BN_3 plane by 32.8°. Despite this twist the B–N bond length suggests considerable boron-nitrogen π bonding. Dewar and Rona have suggested that nitrogen need not be planar for effective π bonding with boron.[10]

For the monoalkylaminoboranes (series I), as the size of the alkyl group increases from methyl (−24.6 ppm) to ethyl (−23.6 ppm) to *n*-propyl (−23.3 ppm) to isopropyl (−22.4), the boron chemical shift increases. Clearly this is opposite to what might be predicted if steric interactions were important in determining the chemical shift of boron. An increase in the electron density on nitrogen as a result of the inductive effect of the alkyl group will result in greater shielding of boron and therefore explains this apparent anomaly.[11] This explanation is supported by the correlation (correlation coefficient 0.976) obtained by plotting the ^{11}B chemical shifts of Ia–d *vs.* Taft σ^*[12] values (see Figure 1).

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(5) J. K. Ruff, *J. Org. Chem.*, **27**, 1020 (1962).

(6) F. A. Davis, M. J. S. Dewar, and R. Jones, *J. Amer. Chem. Soc.*, **90**, 706 (1968).

(7) J. P. Onak, H. Landesman, R. E. Williams, and I. Shapiro, *J. Phys. Chem.*, **63**, 1533 (1959).

(8) E. L. Eliel and M. C. Knoeber, *J. Amer. Chem. Soc.*, **90**, 3444 (1968).

(9) A. H. Clark and G. A. Anderson, *Chem. Commun.*, 1082 (1969).

(10) M. J. S. Dewar and P. Rona, *J. Amer. Chem. Soc.*, **91**, 2259 (1969).

(11) It should be noted that this trend is opposite to that observed for the pK_a's of monoalkylamines and has been attributed to steric hindrance to solvation: see H. K. Hall, Jr., *ibid.*, **79**, 5441 (1957).

(12) R. W. Taft, Jr., in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., Wiley, New York, N. Y., 1956.

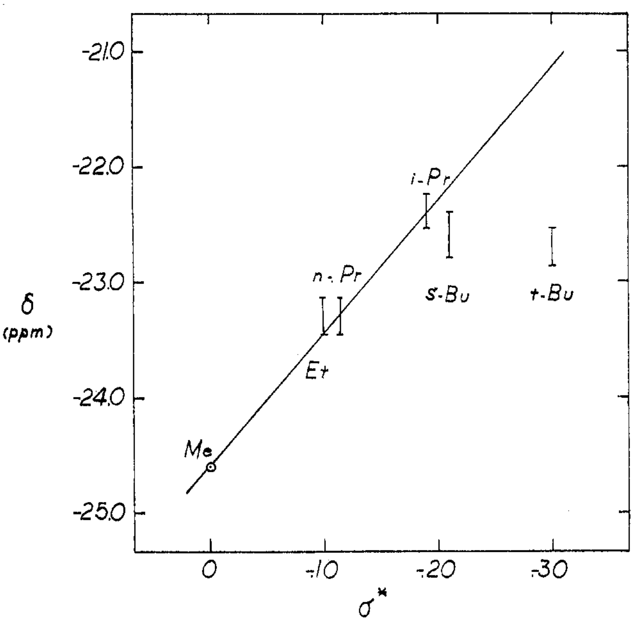

Figure 1.—Plot of the ^{11}B chemical shifts of series I *vs.* σ^*.

Methyl (Ia), ethyl (Ib), *n*-propyl (Ic), and isopropyl (Id) correlate reasonably well, but *sec*-butyl (Ie) and *tert*-butyl (If) do not. Apparently nonbonded interactions between the alkyl groups are important in Ie–f resulting in reduced shielding of boron.

The trisdialkylaminoboranes (series II) have the same chemical shift and are deshielded by 5–6 ppm as compared with series I. This low field shift for series II may be attributed to increased nonbonded interactions which reduce the coplanarity of the nitrogen and boron orbitals. The substantial twist about the B–N bond in IIa[9] is apparently not increased by increasing the size of the alkyl group in this series.

The clearest example of nonbonded interactions affecting the boron chemical shift is observed for series III. Bisdiisopropylaminoboron chloride (IIIc) is approximately 2 ppm deshielded as compared with IIIa and IIIb. Models (Drieding) suggest that there are considerably fewer nonbonded interactions between the alkyl groups in IIIa than in IIIc.

With the exception of *tert*-butyl borate (IVd), the alkyl borates in series IV have identical boron chemical shifts. The effect of nonbonding interactions between the alkyl groups would be expected to have little effect on the chemical shift not only because they are fewer, but because oxygen has two lone pairs of electrons with which to shield boron.

The large shielding of *tert*-butyl borate (IVd), −15.7 ppm, as compared with the rest of the series, −18.0 ppm, is difficult to explain in terms of the inductive effect of the *tert*-butyl group, since *sec*-butyl borate (IVc) shows no increase in shielding. The shielding of IVd as compared with the rest of the series may be explained either in terms of repulsion between the lone pairs of electrons on oxygen or to a diamagnetic shielding effect of the alkyl groups.

It is well known that repulsions between lone pairs of electrons can be important in determining the conformation of molecules.[13] As already pointed out, the most favorable conformation for shielding of boron by an adjacent atom containing lone pairs of electrons is with the lone pair and the orbital on boron being coplanar. In this conformation the lone pairs of electrons will be eclipsed. By twisting about the B–O bond this unfavorable interaction may be relieved but will result in lower chemical shifts for the borates. However, in compound IVd repulsions between the alkyl groups may be more important than repulsion between the lone pairs of electrons, resulting in a more effective B–O π bond and hence great shielding.[14] The greater shielding of IVd may also be due to diamagnetic shielding by the alkyl groups. Models suggest that there is a close proximity between the alkyl groups in IVd and the p_z orbital on boron.

In conclusion, these results indicate that inductive effects and conformation of groups attached to boron have a measurable effect on the ^{11}B chemical shift.

Experimental Section

The borates and aminoboranes were prepared according to procedures given in the literature. Purity was checked by glc. ^{11}B nmr chemical shifts were measured with a Varian HR-100 at 32.1 MHz reference against a capillary containing boron trifluoride etherate.

Registry No.—Ia, 7397-44-6; Ib, 4254-92-6; Ic, 28049-70-9; Id, 22238-43-3; Ie, 28049-72-1; If, 18379-73-2; IIa, 4375-83-1; IIb, 867-97-0; IIc, 20708-66-1; IId, 13006-02-5; IIIa, 6562-41-0; IIIb, 868-25-7; IIIc, 28049-80-1; IVa, 688-74-4; IVb, 13195-76-1; IVc, 22238-17-1; IVd, 7397-43-5; IVe, 621-78-3; IVf, 4396-02-5; IVg, 5456-06-4.

Acknowledgment.—We are indebted to Dr. Ben A. Shoulders, University of Texas, for running the boron spectra and to Dr. R. O. Hutchins for helpful discussions.

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[13] (a) E. L. Eliel, *Accounts Chem. Res.*, **3**, 1 (1970); (b) R. O. Hutchins, L. D. Kopp, and E. L Eliel, *J. Amer. Chem. Soc.*, **90**, 7174 (1968).

[14] Nonbonded interactions between the lone pair electrons in aminoboranes I–III undoubtedly occur, but their effect on the boron chemical shift is difficult to determine. The major factor appears to be interaction between the alkyl groups.

Crystal State Photodimerization of Methyl α-(4-Nitrophenyl)acrylate and 4-Nitrostyrene

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Several reports, especially the elegant studies of Schmidt and coworkers, have shown that cyclobutanes obtained by crystal state photodimerization can be expected to arise by a lattice-controlled stereospecific process.[2,3] Our interest in this topic prompted us to examine the photochemical behavior of some crystalline α-(4-substituted phenyl)acrylic acids and esters.

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[1] (a) Abstracted in part from the M.S. Thesis of E. Hertz, Villanova University, May 1968; (b) National Science Foundation Undergraduate Participant, academic year 1966–1967 and summer 1967 (Grant No. GY-41 and GY-2669).

[2] M. Lahav and G. M. J. Schmidt, *J. Chem. Soc., B*, 239 (1967), and preceding papers in that series.

[3] D. J. Trecker in "Organic Photochemistry," Vol. 2, O. L. Chapman, Ed., Marcel Dekker, New York, N. Y., 1969, p 63.