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Carbon-13 Nuclear Magnetic Resonance Studies of Trimethylamine Adducts of the Mixed Trihalides of Boron

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Received July 2, 1975

AIC50466K

Carbon-13 NMR spectra have been obtained for trimethylamine adducts of the mixed trihalides of boron, $\text{Me}_3\text{N}\cdot\text{BX}_n\text{Y}_{3-n}$ ($n = 0-3$, X and Y are halogens, F, Cl, Br, and I). The $\delta(^{13}\text{C})$ moves downfield on substitution of heavier halides, the shifts reflecting the order of Lewis acidity. Linear correlations are obtained between $\delta(^{13}\text{C})$ and (a) the corresponding proton chemical shifts, (b) the ^{11}B complexation shifts, and (c) $J_{^{11}\text{B}-^{19}\text{F}}$ showing that the ^{13}C shifts reflect the changes in the B-N bond. From the regression line, NMR parameters of unobserved species may be calculated. No coupling of carbon to ^{11}B is noted, while fluorine-containing adducts have broadened peaks as a result of unresolved $J_{^{13}\text{C}-^{19}\text{F}}$ couplings. Both the ^{13}C and corresponding ^1H chemical shifts show pairwise additivity with respect to halogen substitution about boron.

Introduction

Although ^{13}C NMR has not been extensively applied to studies of adducts, recent work by Fratiello et al.¹ has shown that the ^{13}C NMR chemical shifts of the α carbons of several ethers gave downfield shifts on coordination to BF_3 or BCl_3 , the stronger acceptor, BCl_3 , causing the greater shift. They concluded that $\delta(^{13}\text{C})$ for the α carbon reflected electron density shifts on complexation, essentially a diamagnetic term. They also reported the β and γ shifts to be in the opposite direction, a paramagnetic term now being predominant. Subsequently, Geanangel² reported the ^{13}C NMR spectra of trimethylamine-boron adducts, $\text{Me}_3\text{N}\cdot\text{BH}_n\text{F}_{3-n}$ ($n = 1-3$) and $\text{Me}_3\text{N}\cdot\text{BX}_3$ (X = F, Cl, Br). The shifts observed for the trihalides give the same order of Lewis acidity as is obtained from ^1H NMR and thermodynamic measurements.^{3,4} A good correlation was also reported between $\delta(^{13}\text{C})$ and $\Delta\delta(^{11}\text{B})$, the boron complexation shift. Although not pointed out by Geanangel, there is not a simple downfield shift of the ^{13}C resonance on complexation, the shift being slightly upfield for BF_3 and downfield for both BCl_3 and BBr_3 , only the order of shifts for the complexes and not their position relative to free trimethylamine being important.

Having previously reported ^1H , ^{19}F , and ^{11}B data on the trimethylamine adduct of the mixed trihalides of boron⁴⁻⁷ (a total of 20 complexes) we now report the nature of their ^{13}C NMR spectra.

Experimental Section

Mixed adducts were prepared in CDCl_3 solution as described previously.⁴ ^{13}C NMR data were obtained in CDCl_3 solution at 33°C in 10-mm tubes using a Bruker WP-60 FT NMR spectrometer operating at 15.08 MHz. Typical spectrometer parameters were a sweep width of 1875 Hz (to include the TMS reference) and an acquisition time of 2.18 sec for an 8K FID. FID's were obtained in the autorecur mode using 30° pulses (3.1 μsec), 1000-16000 pulses (depending on concentration) being accumulated using the PAPS sequence with 5 W of proton noise decoupling. The 4K transformed spectra had only minimal line broadening applied (0.0-0.5 Hz). The chemical shifts were not particularly susceptible to either concentration (0.1 mole % to saturated, the heavier halide adducts being less soluble), the presence of more than one adduct in solution, or the presence of an excess of free Lewis acid in solution. The average standard deviation in shifts over this wide variety of conditions was ± 1.0 Hz (0.07 ppm),

while for the worst cases, the sparingly soluble iodide-containing adducts, precision was still ± 1.5 Hz (± 0.1 ppm). Shifts were measured by interpolation on the plotted spectra, by the cursor routine available through the computer, and via the plot/list routine. Resolution was typically better than 1 Hz, often single channel for TMS and CDCl_3 peaks, but the adduct peaks were broadened.

No attempt was made to observe the ternary adducts such as $\text{Me}_3\text{N}\cdot\text{BFCIBr}$ since their low concentrations would have required exceedingly long accumulation times.

Pairwise parameters were calculated as described previously.⁶ Linear regressions were carried out on a Wang 2200 programmable calculator which provided the intercept *A*, slope *B*, correlation coefficient *r*, standard errors of estimate, and calculated points based on the regression line.

Results and Discussion

I. Carbon-13 Chemical Shift. The results of the ^{13}C chemical shift measurements are shown in Table I which lists the adducts in order of increasing methyl proton chemical shifts. These have previously been taken as a measure of the relative order of acceptor power of the boron trihalide.^{3,4} Unlike the proton case, there is not an immediate downfield shift of the methyl carbons on adduct formation. The weakest adduct, $\text{Me}_3\text{N}\cdot\text{BF}_3$ is in fact observed at a somewhat higher field than that of free trimethylamine. Chemical shifts however decrease regularly on substitution of heavier halogens, the order essentially paralleling that observed for protons except for three pairs of adjacent adducts, D-BBr₂I and D-BCl₂I₂, D-BClBr₂ and D-BCl₂I, and D-BCl₂Br and D-BFI₂ whose order of carbon shifts is inverted from that observed with proton spectra. All three pairs involve iodine-containing adducts, which for solubility reasons have the greatest experimental errors, and the shift differences between the adducts concerned are within the carbon and proton experimental error. Unlike hydrocarbons, there is no upfield ^{13}C shift associated with the presence of iodine atoms.

Since essentially the same order is obtained for $\delta(^{13}\text{C})$ and $\delta(^1\text{H})$, it would appear that both measurements reflect the same property of the adducts. This is further borne out by Figure 1, a plot of $\delta(^1\text{H})$ vs. $\delta(^{13}\text{C})$ which surprisingly shows a very linear relationship (correlation coefficient $r = 0.991$) with the greatest deviations occurring for the iodide-containing adducts. If these are omitted, an even better fit is obtained

Table I. Observed and Calculated Proton and Carbon-13 Chemical Shifts, Boron-11 Complexation Shifts, and B-F Coupling Constants of Trimethylamine-Boron Trihalide Adducts

Adduct	$\delta(^1\text{H})^a$		$\delta(^{13}\text{C})^d$				$\Delta\delta(^{11}\text{B})^h$		$J^{11}\text{B}-^{19}\text{F}^j$	
	Obsd ^b	Calcd ^c	Obsd	Calcd ^e	Calcd ^f	Calcd ^g	Obsd	Calcd ⁱ	Obsd ^b	Calcd ^h
Me ₃ N (free in CDCl ₃)	2.20		47.72							
Me ₃ N·BF ₃	2.60	2.60	47.13	47.30	47.13	47.09	8.8	10.1	15.1	19.7
Me ₃ N·BF ₂ Cl	2.71	2.71	47.85	48.03	47.91	47.86	17.4	16.8	45.5	40.8
Me ₃ N·BF ₂ Br	2.75	2.75	48.22	48.29	48.19	48.25		20.2	53.8	51.6
Me ₃ N·BF ₂ I	2.77	2.77	48.60	48.43	48.33	48.67		23.7		62.7
Me ₃ N·BFCl ₂	2.83	2.84	48.75	48.82	48.75	48.74	25.5	25.1	64.5	67.1
Me ₃ N·BFClBr	2.89	2.89		49.22	49.17	49.19		29.0	78.0	79.4
Me ₃ N·BFClI	2.92	2.91		49.41	49.38	49.67		31.0		85.6
Me ₃ N·BFBr ₂	2.93	2.93	49.56	49.48	49.45	49.53		32.6	89.6	90.9
Me ₃ N·BFBrI	2.97	2.97		49.74	49.73	49.91		34.2		95.8
Me ₃ N·BCl ₃	2.98	2.98	49.76	49.81	49.80	49.76	36.3	34.5		
Me ₃ N·BFCl ₂ Br	3.02	3.02	50.36	50.07	50.08	50.29		40.1		114.3
Me ₃ N·BCl ₂ Br	3.05	3.04	50.22	50.27	50.29	50.25		38.8		
Me ₃ N·BCl ₂ I	3.08	3.08	50.81	50.47	50.50	50.78		44.2		
Me ₃ N·BClBr ₂	3.09	3.10	50.67	50.54	50.58	50.64		42.9		
Me ₃ N·BClBrI	3.14	3.15		50.87	50.92	51.09		45.1		
Me ₃ N·BBr ₃	3.15	3.15	50.94	50.93	51.00	50.94	43.9	45.4		
Me ₃ N·BCl ₂ I	3.20	3.20	51.47	51.26	51.35	51.50		50.3		
Me ₃ N·BBr ₂ I	3.21	3.21	51.19	51.33	51.42	51.26		47.8		
Me ₃ N·BBrI ₂	3.28	3.28	51.66	51.79	51.91	51.59		52.1		
Me ₃ N·BI ₃	3.35	3.35	51.89	52.25	52.40	51.93		54.2		

^a Ppm downfield of TMS. ^b From ref 4. ^c Calculated using the $\delta(^1\text{H})$ pairwise additivity parameters from Table II (standard error ± 0.005 ppm). ^d Ppm downfield of TMS—this work. ^e Calculated from the ^1H vs. ^{13}C regression line—all data included ($r = 0.991$, standard error ± 0.19). ^f Calculated from the ^1H vs. ^{13}C regression line; iodine-containing species omitted ($r = 0.999$, standard error ± 0.07). ^g Calculated using the $\delta(^{13}\text{C})$ pairwise additivity parameters from Table II (standard error ± 0.04 ppm). ^h Complexation shift in ppm; observed values from ref 8. ⁱ Calculated values based on the $\delta(^{13}\text{C})$ vs. $\Delta\delta(^{11}\text{B})$ regression line ($r = 0.995$, standard error ± 1.6). ^j In Hz. ^k Calculated from the $\delta(^{13}\text{C})$ vs. $J^{11}\text{B}-^{19}\text{F}$ regression line ($r = 0.991$, standard error ± 3.7).

($r = 0.999$). In Table I, $\delta(^{13}\text{C})$ values calculated from these regression lines are included.

It would appear that an upfield contribution to $\delta(^{13}\text{C})$ arises from coordination of the boron to the nitrogen, as seen from the upfield shift of the weakest adduct Me₃N·BF₃. There is then a monotonic downfield shift on substitution of heavier halogens. The downfield shift from Me₃N·BF₃ might then be considered a measure of the changing diamagnetic term as are the proton shifts for these compounds, i.e., the nature of the electron-withdrawing effect of the acceptor molecules.

It would thus appear that the ^{13}C chemical shift does, in this closely related series, mirror the order of acceptor power of the boron trihalides. Such conclusions must be drawn with care as pointed out by Geanangel,² who observed the corresponding data for Me₃N·BH_nF_{3-n} ($n = 0-3$) for which the proton and carbon orders do not agree. Whereas the proton data suggest Me₃N·BF₃ and Me₃N·BH₃ are similar acceptors, the carbon data would indicate that BH₃ is a stronger acceptor than even BI₃. However, since the proton data for the BHF₂ and BH₂F adducts are also anomalous, it would appear that the presence of hydrogen on boron introduces strong effects. This has previously been observed⁹ with respect to the pairwise treatment⁶ of NMR data for haloborane adducts and BH₄⁻, and since, as shown below, $\delta(^1\text{H})$ and $\delta(^{13}\text{C})$ show pairwise behavior, then these anomalies would not be unexpected.

Surprisingly, there is little effect on $\delta(^{13}\text{C})$ caused by concentration changes, the presence of more than one adduct, or even large excesses of free Lewis acid, since Geanangel observed relatively large solvent shifts (≈ 1.5 ppm upfield) on changing from CDCl₃ to a CDCl₃-CH₃CN mixed solvent. We were unable to investigate this mixed-solvent system since the rapid preparation of mixed adducts involves the presence of excess free Lewis acid which would couple with the CH₃CN.

Unfortunately, no $^{13}\text{C}-^{11}\text{B}$ or $^{13}\text{C}-^{19}\text{F}$ coupling was observed, despite the fact that carbon is one bond closer than the protons for which $J_{\text{H-B}}$ also parallels the strength of the B-N bond. Geanangel² has observed poorly resolved carbon-fluorine couplings for both the BHF₂ and BH₂F adducts, (≈ 2.4 and 2.0 Hz, respectively), but not for the BF₃ adduct.

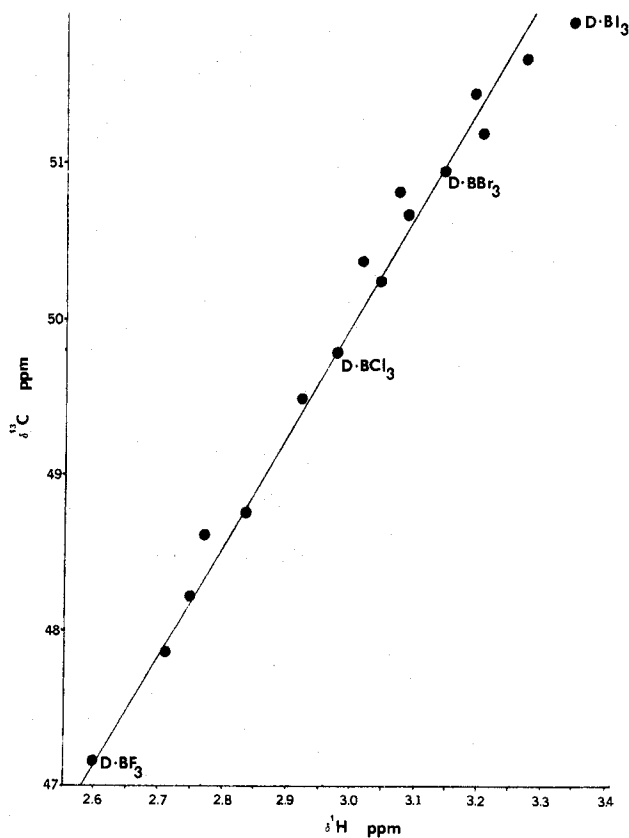


Figure 1. Plot of $\delta(^{13}\text{C})$ for Me₃N·BX_nY_{3-n} (X and Y are halogens, $n = 0-3$): $A = 28.88$, $B = 7.021$ (iodide adducts omitted); $A = 20.15$, $B = 6.597$ (all adducts).

Our results are similar, none of our ten fluorine-containing adducts showing observable couplings, although line widths were slightly greater for these adducts compared to non-fluorinated species in the same sample.

II. Correlation with ^{11}B Complexation Shifts and $^{11}\text{B}-^{19}\text{F}$

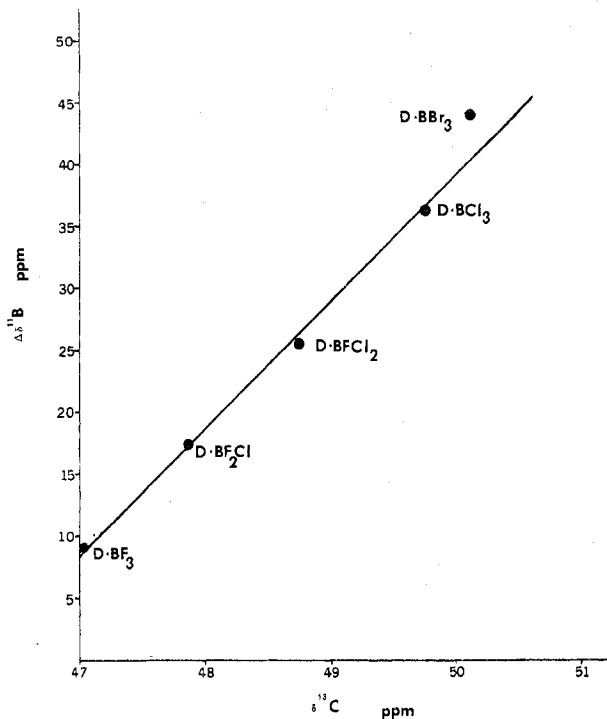


Figure 2. Plot of $\delta(^{13}\text{C})$ vs. $\Delta\delta(^{11}\text{B})$ for $\text{Me}_3\text{N}\cdot\text{BX}_n\text{Y}_{3-n}$ (X and Y are halogens, $n = 0-3$): $A = 427.08$, $B = 9.276$.

Coupling Constants. Boron-11 chemical shifts do not reflect the order of acceptor power of the boron trihalides, although the pairwise additivity parameters contributing to these shifts appear to correlate with the hard or soft nature of the substituent.⁶ Complexation shifts, $\Delta\delta(^{11}\text{B})$, the difference in chemical shift between free and coordinated BX_3 have been related to adduct strengths.¹⁰ Geanangel reported a linear correlation for $\delta(^{13}\text{C})$ vs. $\Delta\delta(^{11}\text{B})$, and we observe a similar relationship using our ^{13}C data, the mixed-adduct ^{11}B data of Binder and Fluck,⁸ and the free halide data from Eaton and Lipscomb.¹¹ The correlation with $\Delta\delta(^{11}\text{B})$ ($r = 0.995$) is linear (Figure 2) and the calculated ^{11}B complexation shifts are shown in Table I including those adducts whose ^{11}B spectra have not been investigated.

Similarly, $J_{^{11}\text{B}-^{19}\text{F}}$ has been shown to reflect the Lewis acid strength of the fluorine-containing boron trihalides (Table I), and, again, a linear correlation ($r = 0.991$) is shown between $\delta(^{13}\text{C})$ and $J_{^{11}\text{B}-^{19}\text{F}}$ (Figure 3). We thus have four independent NMR measurements (two chemical shifts, a complexation shift, and a coupling constant) not only reflecting the relative acceptor roles of the boron trihalides and mixed trihalides but also being linearly related, thus suggesting a measurement of the same property. The fifth available NMR parameter, $\delta(^{19}\text{F})$,⁴ again reflects the same ordering, but not so linear a relationship ($r = 0.956$). As the proton chemical shifts have previously been shown to correlate with heats of complexation and other physical measurements of acceptor strength,³ it can be concluded that these other NMR measurements also reflect the properties of the B-N bond. Work is presently under way in an attempt to obtain ^{15}N NMR data for these systems which would complete the NMR study of the $\text{Me}_3\text{N}\cdot\text{BX}_3$ system with the exception of the more difficult studies of the heavier halogens.

III. Pairwise Additivity: $\delta(^{13}\text{C})$ and $\delta(^1\text{H})$. Pairwise interaction¹² of directly bonded substituents about the central atom has been demonstrated for ^{19}F , ^{11}B , ^{13}C , ^{27}Al , ^{93}Nb , and other chemical shifts and for directly bonded couplings $J_{\text{C-F}}$, $J_{\text{Si-H}}$, $J_{\text{Sn-H}}$, $J_{\text{B-F}}$, and other systems,^{6,13-18} the $\delta(^{19}\text{F})$ data being the only case where one of the atoms observed was not

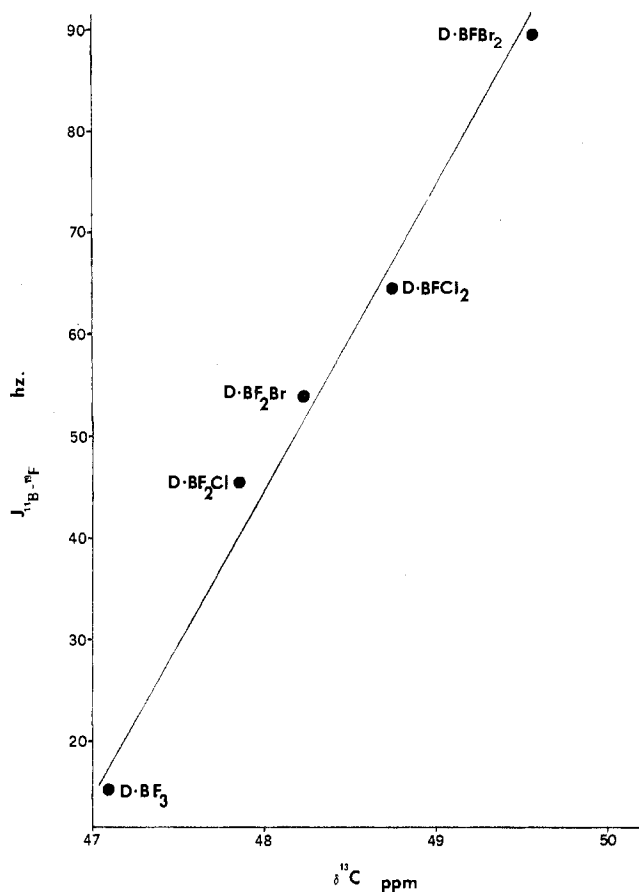


Figure 3. Plot of $\delta(^{13}\text{C})$ vs. $J_{^{11}\text{B}-^{19}\text{F}}$ for $\text{Me}_3\text{N}\cdot\text{BX}_n\text{Y}_{3-n}$ (X and Y are halogens, $n = 0-3$): $A = -1360$, $B = 29.28$.

Table II. Pairwise Interaction Parameters of $\delta(^1\text{H})$ and $\delta(^{13}\text{C})$

X-X	$\eta(^1\text{H})$, ppm	$\eta(^{13}\text{C})$, ppm	X-X	$\eta(^1\text{H})$, ppm	$\eta(^{13}\text{C})$, ppm
F-F	0.8669	15.699	Cl-Br	1.024	16.831
F-Cl	0.9210	16.079	Br-Br	1.049	16.979
F-Br	0.9411	16.276	Cl-I	1.042	17.099
F-I	0.9518	16.488	Br-I	1.080	17.140
Cl-Cl	0.9958	16.587	I-I	1.117	17.309

the central atom. If we treat either $\delta(^1\text{H})$ or $\delta(^{13}\text{C})$ of adducted trimethylamine as the chemical shift of the donor, D, in, for example, the complex $\text{D}\cdot\text{BF}_2\text{Cl}$, then by the pairwise additivity criterion

$$\delta_{\text{donor}} = \eta_{\text{FF}} + 2\eta_{\text{F-Cl}}$$

where the η 's are the pairwise interaction parameters.

Both the carbon-13 and proton shifts were subjected to a least-squares fit to the pairwise criterion, the pairwise interaction parameters determined being shown in Table II. Table I shows $\delta(^1\text{H})$ and $\delta(^{13}\text{C})$ calculated from these parameters, the standard errors of ± 0.005 and ± 0.04 ppm, respectively, being less than the corresponding experimental errors. Thus, excellent fits for pairwise substitution about boron are obtained, not just for an atom directly bonded such as fluorine but for atoms $\beta(^{13}\text{C})$ and $\gamma(^1\text{H})$ to the boron, without any significant attenuation of the effect. This pairwise additivity of proton shifts in adducts applies to aromatic protons also, the 2,6 protons of the 4-Mepy-BX₃ adducts showing the same behavior.⁹

We have previously shown⁶ that for $J_{^{11}\text{B}-^{19}\text{F}}$ the pairwise additivity parameters η_{XY} could be correlated with both the sum of the electronegativities of X and Y and the sum of the van der Waals radii of X and Y. Such a linear relationship also holds for the pairwise parameters obtained from $\delta(^{13}\text{C})$

and $\delta(^1\text{H})$, the correlation coefficient being for the van der Waals radii $r^{13\text{C}} = 0.995$ and $r^{1\text{H}} = 0.988$, while for electronegativities $r^{13\text{C}} = 0.990$ and $r^{1\text{H}} = 0.980$. The van der Waals radius correlation may suggest a very subtle steric effect, but the B–N bond is the strongest in the case of $\text{Me}_3\text{N}\cdot\text{BI}_3$, the sterically most crowded structure.

The extent of the NMR and other interrelations suggests that the $\text{Me}_3\text{N}\cdot\text{BXYZ}$ (X, Y, and Z are halogens) system would be appropriate for theoretical study in order to account for these phenomena. Of particular interest would be the anomalous behavior of the NMR parameters of trimethylamine–borane and –haloborane adducts.

Acknowledgment. The authors wish to thank the National Research Council of Canada for financial support.

Registry No. $\text{Me}_3\text{N}\cdot\text{BF}_3$, 420-20-2; $\text{Me}_3\text{N}\cdot\text{BF}_2\text{Cl}$, 25889-87-6; $\text{Me}_3\text{N}\cdot\text{BF}_2\text{Br}$, 25889-93-4; $\text{Me}_3\text{N}\cdot\text{BF}_2\text{I}$, 25889-95-6; $\text{Me}_3\text{N}\cdot\text{BFCl}_2$, 25889-88-7; $\text{Me}_3\text{N}\cdot\text{BFClBr}$, 39708-26-4; $\text{Me}_3\text{N}\cdot\text{BFClI}$, 39708-27-5; $\text{Me}_3\text{N}\cdot\text{BFBr}_2$, 25889-94-5; $\text{Me}_3\text{N}\cdot\text{BFBrI}$, 39708-28-6; $\text{Me}_3\text{N}\cdot\text{BCl}_3$, 1516-55-8; $\text{Me}_3\text{N}\cdot\text{BFI}_2$, 25889-96-7; $\text{Me}_3\text{N}\cdot\text{BCl}_2\text{Br}$, 25889-90-1; $\text{Me}_3\text{N}\cdot\text{BCl}_2\text{I}$, 25889-97-8; $\text{Me}_3\text{N}\cdot\text{BClBr}_2$, 25889-91-2; $\text{Me}_3\text{N}\cdot\text{BClBrI}$, 39708-29-7; $\text{Me}_3\text{N}\cdot\text{BBR}_3$, 1516-54-7; $\text{Me}_3\text{N}\cdot\text{BClI}_2$, 25889-98-9;

$\text{Me}_3\text{N}\cdot\text{BBR}_2\text{I}$, 39708-24-2; $\text{Me}_3\text{N}\cdot\text{BBR}_2\text{I}_2$, 39708-25-3; $\text{Me}_3\text{N}\cdot\text{BI}_3$, 5041-59-8; ^{13}C , 14762-74-4; ^{11}B , 14798-13-1.

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Use of Pseudopotential Theory to Study Molecular Structure. II. A NOCOR (Neglect of Core Orbitals) Calculation of the P₄ and P₂ Molecules and Their Interconversion

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Received July 14, 1975

AIC50493A

The new (NOCOR) valence-only ab initio LCAO–MO–CSF method, in which the effect of the core electrons is represented by a local model potential and a nonlocal pseudopotential, has been applied to the P₂ and P₄ molecules and is found to give results for a minimum-Slater representation (in which only s and p atomic functions are employed) that are comparable to those from full-core calculations. Optimization of the molecular geometry for this representation also leads to good results. Upon adding d functions, it is found that the electronic hybridization of each phosphorus atom in the P₄ molecule goes from $s^{1.90}p^{3.10}$ to $s^{1.77}p^{3.08}d^{0.15}$, resulting in considerable polarization of the valence electronic distribution with the total electronic charge shifting away from the atoms into the center of the P₄ tetrahedron and also into the P–P axial regions. The enthalpy and an activation energy have been calculated for a symmetry-allowed dissociation of P₄ into 2P₂, a process which was followed in detail with bond distance optimization.

Introduction

There are still many problems, covering the full range from preparative through theoretical chemistry, concerned with the variety and structures of the allotropic forms¹ of phosphorus. For example, the role of d atomic orbitals in the electronic structure of the P₄ tetrahedral molecule has been a central issue discussed in two recent papers^{2–4} describing ab initio SCF computations on this molecule. However the size of the basis set required for inclusion of d character was sufficiently large so as to be precluded from actual calculation in both papers. Our recently developed^{5–7} NOCOR procedure for carrying out ab initio SCF computations for only the valence orbitals offers a way of readily incorporating⁵ d character into the LCAO description of the P₄ molecule and such work is reported herein.

Although there is a near-Hartree–Fock computation⁸ available for the P₂ molecule, the relationship between the electronic structures of the P₂ and P₄ molecules has not been investigated previously. Therefore we have recalculated the P₂ molecule in a valence-only minimum-Slater basis set and have mathematically simulated the process of pulling apart a P₄ molecule into two P₂ molecules in a symmetry-allowed fashion.

Computational Details

The previously described^{5–7} procedure was employed for carrying out LCAO–MO–SCF computations on the valence

orbitals of the molecules under study, using an adaptation of the Phillips–Kleinman pseudopotential to replace orthogonality constraints along with an exponential screening function to replace the core–valence Coulombic and exchange interactions. An atom-optimized⁹ minimum-Slater basis set in which each orbital was described by three Gaussian functions,¹⁰ i.e., STO-3G, was employed; and, for introducing d character, a sixfold single-Gaussian set of d functions was used with an exponent chosen as previously described.¹¹ A Slater function expressed in terms of six Gaussian functions was used to delineate each atom symmetry type in the core; but, of course, these core functions are not part of the basis set since they serve only to define the pseudopotential.

Results and Discussion

NOCOR vs. Full SCF. Since the NOCOR method is still quite new, we believe it is desirable to compare the results obtained with it to those from regular full-SCF calculations, particularly when about the same basis set was employed. In Table I a series of properties is reported for the P₂ molecule using the NOCOR method, a reasonably comparable minimum-Slater calculation,^{12,13} and a near-Hartree–Fock computation.⁸ A similar comparison for the P₄ molecule of the NOCOR results with minimum-Slater findings² and the results from a rather large Gaussian calculation⁴ (equivalent to a single- ζ description for the core and a double- ζ description for the valence shell) are reported in Table II. In both tables,