The Microwave Spectrum and Structure of the Unstable Molecule Bromine Isocyanate, BrNCO¹

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The microwave spectra of two isotopic species of the unstable molecule bromine isocyanate, BrNCO, have been observed from the flow reaction of Br_2 vapor with silver cyanate. The spectra were observed in the frequency range 8-54 GHz. They contain strong *a*-type transitions, as well as *b*-type transitions, with the latter so weak they initially could not be assigned. The transitions show Br and N quadrupole hyperfine structure; many perturbations in the former have been found, and have been used in a novel method to evaluate accurately *all* the rotational constants and the Br quadrupole coupling tensor entirely from *a*-type *R* branches. This has been done using a global least-squares fitting program developed especially for the purpose. The resulting constants permitted the *b*-type transitions to be identified. The molecule has been shown to be planar, the BrNCO configuration has been confirmed, and a partial r_0 structure has been determined. The principal values of the Br quadrupole tensor have been evaluated and the Br—N bond has been shown not to be bent. @ 1986 Academic Press, Inc.

INTRODUCTION

Isocyanates, which contain the -NCO group, are examples of a class of molecules known as pseudohalides, substances with similar chemical properties to the halides. Other examples include the azides, thiocyanates, and cyanides. The structures of many volatile pseudohalides have been determined by both electron diffraction and micro-wave spectroscopy (1-4), and have often been found to have interesting features. The thiocyanates, for example, may be linked to the remainder of the molecule via either S (thiocyanates) or N (isothiocyanates); there seems to be no a priori indication which will prevail for a given substituent. All known cyanates, on the other hand, are isocyanates, linked via N; the X-N-C angle, however, varies widely, depending on X, from effectively 180° in SiH₃NCO (2), to 118° in CINCO (3, 4). In addition, in CINCO the NCO chain is itself nonlinear, with the O atom bent away from the N-C axis by $\sim 9^\circ$, in a *trans* configuration to Cl (3, 5).

No structural data have been previously determined for bromine isocyanate, BrNCO. This molecule was first prepared by Gottardi, by the reaction of Br_2 vapor with AgNCO (6), and by the vacuum thermolysis of tribromoisocyanuric acid (7). Its infrared spectra in both the solid and gas phases have been reported (7), as has its He(I) photoelectron spectrum (8).

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¹ Work supported by the Natural Sciences and Engineering Research Council of Canada.

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This paper presents the microwave spectra of two isotopic species of BrNCO; a preliminary account has been given earlier (9). Considerable structural information has been deduced from the derived constants. The transitions show very large Br quadrupole splittings, which have permitted development of a novel procedure for obtaining accurate values for rotational constants which might otherwise be unavailable.

EXPERIMENTAL METHODS

Bromine isocyanate was prepared in a flow system by passing Br_2 over heated silver cyanate at 150°C at a pressure of 30 mTorr (6, 9). AgNCO had previously been prepared by the reaction of KNCO and AgNO₃. It was dried thoroughly under vacuum at 150°C for several hours; this step is very important because BrNCO hydrolyzes easily (7).

The effluent from the reaction zone was pumped continuously through the 6-ft Hewlett-Packard X-band Stark cell of a 100-kHz Stark-modulated spectrometer. The cell was held at room temperature. Measurements were made in the frequency region 8-54 GHz. The fundamental source was a Watkins-Johnson 1291A microwave synthesizer operating from 8-18 GHz. Power above 18 GHz was obtained by multiplying the synthesizer output with Honeywell-Space Kom 14-27 and $T-K_a$ 1 Multipliers. Estimated measurement accuracies were better than ± 0.05 MHz.

OBSERVED SPECTRUM AND ANALYSIS

(a) Initial Assignments

A preliminary calculation of the rotational constants of both ⁷⁹BrNCO and ⁸¹BrNCO was made using structural parameters transferred from ClNCO along with a Br-N bond length shortened somewhat from that of BrNO (10). Br quadrupole coupling constants were estimated from the equations of Townes and Dailey (11), using 4p orbital populations from a CNDO calculation.

The molecule was expected to be a planar near-symmetric prolate rotor, probably having both *a*- and *b*-type transitions. A preliminary inspection of the spectrum showed only a series of equally spaced groups of lines (Fig. 1), easily assigned as *a*-type *R* branches spaced by $\sim (B + C)$. Each group was complicated by the presence of the two isotopes, each with transitions in the ground and several excited vibrational states. In addition each transition showed the anticipated large Br quadrupole splitting.



FIG. 1. Broadband scan of the microwave spectrum of BrNCO, in the frequency range 32.7-38.6 GHz.



FIG. 2. A scan of the $J = 6 \leftarrow 5$ a-type R branch of BrNCO in the frequency range 24.8-26.2 GHz. Transitions are indicated for both isotopic species in the ground and two excited vibrational states.

The first assignments of individual lines were made for $J = 6 \leftarrow 5$, which is shown in Fig. 2. The $K_a = 0$ and 1 transitions were easily distinguished using their positions and Stark effects, for the ground and at least two excited vibrational levels. Similar assignments to other values of J were straightforward. Preliminary values of B and C were obtained from these lines. For most transitions the Br quadrupole structure could be largely accounted for with first-order theory; several, however, had splitting patterns which initially could not be explained. No ¹⁴N splitting was seen for any *a*-type transitions.

Accurate determination of A was a problem. A rough value can sometimes be obtained from a-type R branches using asymmetry splittings of $K_a = 2$ transitions. However, these lines were difficult to assign because of their large quadrupole splittings, and were difficult to measure because of lineshape distortion by Stark components. In any case the asymmetry splittings were very small (~20 MHz for $J = 8 \leftarrow 7$), so A could not be obtained accurately via this route. Nor could it be obtained from b-type transitions at this stage; they too were impossible to assign, this time because they were very weak, with large predicted quadrupole splittings, and because of the large number of isotopes and observable vibrational states for the two isotopic species.

(b) Determination of A and the Br Quadrupole Tensor

The A rotational constant was nevertheless evaluated accurately solely from a-type transitions, using a novel method in which the Br quadrupole tensor was obtained at the same time. This was achieved with a simultaneous least-squares fit to the rotational, centrifugal distortion, and Br quadrupole coupling constants; this accounted for the anomalies in the hyperfine structure mentioned above.

For a planar molecule containing a single quadrupolar nucleus, the quadrupolar Hamiltonian can be written as

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$$\mathscr{H}_Q = \chi_{aa}\phi_{Za}^2 + \chi_{bb}\phi_{Zb}^2 + \chi_{cc}\phi_{Zc}^2 + 2\chi_{ab}\phi_{Za}\phi_{Zb} \tag{1}$$

where χ_{fg} is a quadrupole coupling constant and ϕ_{Zg} is the direction cosine between the space-fixed Z axis and the g-principal inertial axis. For a Br-containing molecule the first three terms, which contribute to first order, usually account for most of the hyperfine structure. However, if through the nature of the molecule χ_{ab} is large, the fourth term, which is off-diagonal in the quadrupole tensor and contributes to higher order, may have a significant effect. This is in fact the case with BrNCO, for Br has a large quadrupole moment, and the principal axes of the quadrupolar and inertia tensors are well separated (by ~28°; see below).

The contributions of χ_{ab} are especially large when there are accidental near degeneracies of the correct type, namely where $\Delta F = 0$, $\Delta J = 0$, ± 1 , or ± 2 , and $K_a K_c = eo \leftrightarrow oo$ or $ee \leftrightarrow oe$. Since these near degeneracies depend on all three rotational constants, and to a lesser extent on the centrifugal distortion constants, deviations from a first-order pattern can provide extra information about these constants along with χ_{ab} . Ideally it should be possible to use these perturbations to evaluate rotational constants which are otherwise indeterminate (such as A in the present case). This procedure was previously suggested for *trans*-1-bromopropene (12), but until now its potential had not been fully realized.

To do this we have written a computer program which does a simultaneous leastsquares fit to the rotational, centrifugal distortion, and Br quadrupole coupling constants. The quadrupole matrix elements are those of Benz *et al.* (13). Since in a symmetric rotor basis the terms in χ_{ab} are of the form $\langle J^1, K \pm 1 | \mathscr{H}_Q | J, K \rangle$, the Wang transformation no longer produces a simple factorization. The matrix is diagonal in the total angular momentum quantum number *F*. The submatrices rapidly become very large with increasing *F* since their order is (2F + 1)(2I + 1), and the interactive fitting procedure requires much computer time. As a result the fits were performed using the CRAY-1 Vector Computer of the Atmospheric Environment Service of Environment Canada.

The predicted values of A and χ_{ab} were used to make initial estimates of the perturbed hyperfine patterns. Initial assignments were made to a few transitions on somewhat of a trial and error basis, but once these were confirmed a bootstrap procedure was used in which constants obtained in a given fit were used to predict further transition frequencies, which were then measured and included in a new fit. The values obtained for A and χ_{ab} were well determined (see Table I) and were also essentially uncorrelated (9); the accuracy of A is several orders of magnitude greater than is usually obtained from a-type R branches. B and C, several distortion constants, and the first-order Br quadrupole constants were also well determined, as is shown in Table I.

An energy level diagram for ⁸¹BrNCO is given in Fig. 3, and two of the closest near degeneracies are indicated. These are between $10_{0,10}-9_{1,8}$ (426.34 MHz apart) and $3_{1,3}-5_{0,5}$ (844.13 MHz apart), and cause the largest deviations from a first-order pattern. Measurable shifts were also obtained for transitions to or from many other levels much further apart, such as $7_{1,6}-8_{0,8}$ (6983 MHz apart). In fact, not one of the measured $K_a = 0$ lines was unperturbed, with frequency shifts ranging from 0.5 MHz in $8_{0,8} \leftarrow 7_{0,7}$ to 33 MHz in $10_{0,10} \leftarrow 9_{0,9}$. Illustrations of the observed patterns and energy levels are in Figs. 4 and 5.

TABLE I

Spectroscopic (Constants	of Bromine	Isocyanate
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Parameter	⁷⁹ BrN	<u>co</u>	81Bri	ico			
	<u>a</u> -type transitions ^a	all transitions ^b	a-type transitions ^a	all transitions ^b			
Rotational	constants (MHz)						
Α	41188.71(23) ^c	41189.506(25)	41142.57(39)	41141.914(29)			
B	2175.6311(13)	2175.63391(52)	2159.5035(13)	2159.50429(53)			
с	2063.1025(11)	2063.09857(53)	2048.4716(10)	2048.47014(55)			
Centrifugal	distortion const	ants (kHz)					
Δ.	1.1366(22)	ì.1370(19)	1.1258(23)	1.1281(18)			
Δīν	-172.72(16)	-173.97(14)	-171.00(12)	-172.23(14)			
δτ	0.1692(29)	0.17367(26)	0.1690(26)	0.17004(31)			
^н јкк	—	-0.248(19)		-0.214(19)			
Browing muc	lear quadrunola o	ounling constants	(MHz)				
v	608.16(48)	608,41(52)	508.40(47)	508,49(52)			
^aa ******	279.4(11)	280.086(64)	230.8(11)	233,311(70)			
Xab Acc	549,85(11)	549.67(12)	458.30(22)	458.60(12)			
Nitrogon pu	clear quadrupole	coupling constant	-a (MEFre)				
artrogen du	creat quadrupore	5 09/78)		4.75(51)			
^x aa ^x bb ^{-x} cc	—	1.811(19)		1.912(12)			
Transfel Jefente (n m. 12)							
Δ		0.401		0.401			
Number of r	otational transit 26	ions 43	29	46			
Standard de	viation of distor 0.028	tion fit (MHz) 0.032	0.029	0.034			

^a Ref. (9). These constants were obtained from a-type transitions only. Accurate values of A and X_{ab} were available via a simultaneous least squares fit to rotational, centrifugal distortion and bromine quadrupole constants. ^b These constants were obtained by a least squares fit to all transitions,

both a- and b-type. C Numbers in parentheses are one standard deviation in units of the last

significant figures.

(c) b-Type Transitions and the Final Constants

The constants determined above were used to predict the positions of some $K_a = 1 \leftarrow 0$ b-type lines, which had previously been unassignable because they were very weak. They were found within 1 MHz of the predictions, thus confirming the value for A. Both Q- and R-branch b-type transitions were measured, for J up to 20.

All the *b*-type lines showed 14 N quadrupole splitting; an example is in Fig. 6. Its effect had to be accounted for before the Br coupling constants and rotational constants could be refined further. This was done using a fitting program to the coupling constants of two quadrupolar nuclei, written in the coupling scheme $J + I_{Br} = F_1$; $F_1 + I_N$ = F. This was an excellent approximation for BrNCO, since the N quadrupolar con-

ENERGY LEVELS OF ^{®1}BrNCO



FIG. 3. Rotational energy levels of ⁸¹BrNCO. Two of the most important near degeneracies which influence the Br quadrupole structure are indicated.

stants were much smaller than the Br constants. The fit was done to the N constants using the splittings of lines having the same value of F_1 but differing values of F, and keeping the Br coupling constants fixed. This gave N coupling constants independent of the Br constants; their values are in Table I.

Finally, a complete global fit was made to the rotational, centrifugal distortion, and Br quadrupole constants, including all measured transitions, both a and b type. The fit was done using Watson's A-reduced Hamiltonian in its I' representation (14). Since, unfortunately, only a few branches were observed, only three of the five quartic distortion constants could be included in the fits. These were Δ_J , Δ_{JK} , and δ_J ; Δ_K was assimilated into A. These results are also in Table I, under "all transitions." The measured frequencies, along with the residuals calculated with χ_{ab} omitted and χ_{ab} included are in Tables II and III.

STRUCTURAL PARAMETERS

The spectroscopic constants given in Table I were used to obtain structural information about bromine isocyanate. The inertial defects are small and positive, and are



FIG. 4. The $11_{0,11} \leftarrow 10_{0,10}$ transitions of ⁸¹BrNCO with associated energy levels. (a) The energy levels: (i) the hypothetical unsplit rotational energies; (ii) the bromine quadrupole energy levels as derived from first-order theory, which give the unperturbed transitions of (b); (iii) the bromine quadrupole energy levels as derived from the exact Hamiltonian, with the perturbed transitions of (b). (b) The observed transitions with the calculated first-order and exact Hamiltonian patterns.



FIG. 5. Hyperfine splitting patterns of several $K_a = 0$ transitions of ⁸¹BrNCO.



FIG. 6. The $17_{1,16}$ - $17_{0,17}$ transition of ⁷⁹BrNCO showing each transition of the Br quadrupole pattern split by ¹⁴N nuclear quadrupole effects.

the same for both isotopic species, thus indicating that the molecule is planar. This conclusion is supported by the ratio of the out-of-plane quadrupole constants of the two species $\chi_{cc}(^{81}\text{BrNCO})/\chi_{cc}(^{79}\text{BrNCO}) = 0.8350$; this is very close to the ratio of the quadrupole moments of the Br atoms (0.8354).

The ¹⁴N quadrupole constants confirm that the configuration is BrNCO rather than BrOCN. For the latter case the CN bond is very likely to be a principal axis of the ¹⁴N quadrupole tensor, with component $\chi_{zz} \sim -4$ MHz. The out-of-plane component χ_{cc} would thus be $\sim +2$ MHz if the -CN bond were cylindrically symmetrical, and would still be positive even with quite large asymmetry. The fact that χ_{cc} for N is negative for both isotopes (~ -3.4 MHz) is thus very strong evidence that BrNCO is the correct configuration.

Although we do not have enough isotopic data to obtain definitive values for the bond lengths and angles, some reasonable deductions can nonetheless be made. A least-squares fit was made of the observed rotational constants to the Br-N length and Br-N-C angle. The NC and CO lengths were fixed at their values in ClNCO (4), and three fits were done, varying the NCO angle between 9.13° (as in ClNCO (4)), and 0° (a linear NCO group). Table IV shows the resulting parameters. The BrNC angle is reasonable compared to the ClNC angle in ClNCO (119°22'). The BrN length compares well with BrN bond lengths in other molecules, as is also shown in Table IV.

DISCUSSIONS AND CONCLUSIONS

Aside from the UPS investigation (8), the present work represents the first detailed spectroscopic study of bromine isocyanate. Even so several parameters, notably two quartic centrifugal distortion constants, were unavailable. This was as much a function of the magnitudes of the rotational constants and the weakness of the *b*-type transitions as the instability of the molecule.

Even so this work is a very useful breakthrough in the evaluation of rotational constants which might otherwise be unavailable. The global fitting procedure to combined rotational and quadrupole constants can be applied to quite a large number of molecules. There are restrictions, of course. The procedure is best applied to nuclei

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Transition F' - F"	Normalised ^a Weight	Observed ^b Frequency	Resid Without X _{ab}	uals ^C With X _{ab}
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	³ , ^{1.000} ^{1.000} ^{1.000} ^{1.000}	16697.064 16725.798 16732.136 16747.530	-23.577 -9.839 -0.012 -0.162	-0.082 0.001 -0.006 -0.065
5 1 5 - 11/2 13/2 - 11/2 11/2 - 9/2 7/2 - 5/2 9/2 - 7/2 9/2 - 7/2 11/2 - 11/2 11/2 -	4 1 4 1.000 1.000 1.000 1.000	20907.007 20914.295 20915.140 20922.857	0.769 0.519 0.011 -0.036	0.039 0.028 0.029 0.028
$\begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$	4 0 1.000 1.000 1.000 1.000	21174.479 21185.088 21185.088 21187.013	~20.928 -0.136 0.077 -8.273	-0.058 -0.028 0.052 0.041
5 1 4 - 13/2 - 11/2 7/2 - 5/2 11/2 - 9/2 9/2 - 7/2	4 1 3 2 1.000 2 1.000 2 1.000 2 1.000	21470.377 21474.140 21477.657 21482.051	0.197 -0.019 -0.015 0.128	0.004 -0.005 -0.010 -0.037
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	5,5 2,1.000 2,1.000 2,1.000 2,1.000	25090.043 25094.279 25096.468 25100.904	0.275 0.162 0.020 -0.003	0.036 0.002 0.040 0.044
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	5 0 5 2 0.100 2 0.100 2 1.000 2 1.000	25420.588 25420.588 25436.877 25451.129	-0.183 0.094 9.568 23.585	-0.010 0.073 -0.068 0.062
6 1 5 - 15/2 - 13/2 9/2 - 7/2 13/2 - 11/2 11/2 - 9/2	5 1 4 2 1.000 2 1.000 2 1.000 2 1.000	25766.036 25769.092 25770.035 25773.916	0.310 -0.051 -0.016 0.312	-0.009 -0.031 -0.016 -0.016
7 1 7 - 15/2 17/2 - 15/2 15/2 - 13/2 11/2 - 9/2 13/2 - 11/2	6 1 6 2 1.000 2 1.000 2 1.000 2 1.000	29272.172 29274.880 29277.094 29279.874	0.151 0.099 -0.042 -0.082	0.030 0.018 ~0.021 ~0.045
7 0 7 - 15/2 15/2 - 15/2 15/2 13/2 11/2 - 9/2 13/2 11/2 - 9/2 13/2 - 11/	6 ° ° 2 1.000 2 1.000 2 0.100 2 0.100	29654.116 29654.116 29658.081 29658.504	0.048 -0.286 -0.854 -0.744	0.030 0.018 -0.010 -0.030
7 16 $ 17/2$ $ 15/2$ $11/2$ $ 9/2$ $15/2$ $ 13/2$ $11/2$	6 1 5 2 1.000 2 1.000 2 1.000 2 1.000	30060.726 30062.800 30062.800 30066.356	0.660 -0.048 -0.013 0.686	-0.007 -0.023 -0.024 -0.041

Measured Rotational Transitions (in MHz) of "BrN
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^a Measurements were weighted according to $1/\sigma^2$, where σ is the uncertainty in the measurements. Unit weight corresponded to an uncertainty of 0.03 MHz.

 b Nitrogen hyperfine splitting has been subtracted from the \underline{b} -types.

 $^{\rm C}$ Observed frequency minus the frequency calculated using the constants in Table I.

Transition F' - 1	n F"	Normalised Weight	Observed Frequency	Resid Without X _{ab}	uals With X _{ab}
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	7 /2 /2 /2 /2 /2	1 7 1.000 1.000 1.000 1.000	33453.349 33455.203 33457.276 33459.210	0.067 0.039 -0.020 -0.004	-0.007 -0.010 0.002 0.029
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	7 /2 /2 /2 /2	0.100 0.100 1.000 1.000	33885.400 33885.612 33888.327 33889.384	-0.578 0.023 -0.918 -0.238	0.076 0.006 -0.011 0.002
$\begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$	7 /2 /2 /2 /2	1 6 0.100 0.100 1.000	34355.372 34355.688 34355.688 34360.044	0.081 0.014 2.272 2.450	0.018 0.043 -0.080 -0.044
$\begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$	8 /2 /2 /2 /2	1 8 1.000 1.000 1.000 1.000	37633.739 37635.076 37636.850 37638.241	0.091 0.069 -0.021 -0.012	0.041 0.035 0.003 0.020
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	8 /2 /2 /2 /2	° 8 1.000 0.100 0.100 1.000	38112.998 38114.961 38114.961 38117.988	-2.304 0.101 -2.746 -0.153	0.038 0.086 -0.150 0.023
$\begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$	8 /2 /2 /2 /2	1 7 1.000 1.000 1.000 1.000	38617.849 38626.908 38646.382 38647.578	-31.213 -18.916 -0.800 -0.097	0.0 0.007 -0.054 -0.063
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	9 /2 /2 /2 /2	1 9 1.000 1.000 1.000 1.000	41813.185 41814.197 41815.738 41816.788	0.051 0.032 -0.035 -0.031	0.015 0.009 -0.006 0.003
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	9 /2 /2 /2 /2	os 1.000 1.000 1.000 1.000	42341.688 42345.109 42361.038 42375.034	0.033 0.686 18.890 31.099	0.019 0.009 -0.042 -0.037
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	9 /2 /2 /2 /2	1 B 1.000 1.000 1.000 1.000	42938.775 42938.775 42949.302 42962.772	-0.031 0.473 12.032 22.914	0.014 -0.023 -0.026 -0.030
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	10 /2 /2 /2 /2 /2	1 10 1.000 1.000 1.000 1.000	45991.765 45992.565 45993.878 45994.713	0.049 0.034 -0.035 -0.026	0.021 0.016 0.0 0.014
$\begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$	10 /2 /2 /2 /2	° 10 1.000 1.000 1.000 1.000	46544.577 46554.253 46565.779 46567.612	-23.029 -12.030 0.039 -0.534	-0.014 0.021 0.027 0.010
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	10 /2 /2 /2 /2	0.100 0.100 0.100 0.100 1.000	47228.576 47228.888 47228.888 47228.888 47231.377	0.060 -0.100 1.192 1.555	0.030 -0.032 -0.023 -0.012

TABLE II—Continued

					<u> </u>
Transi F' -	tion F"	Normalised Weight	Observed Frequency	Residu Without X _{ab}	with x _{ab}
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	- 11 25/2 23/2 19/2 21/2	1.000 1.000 1.000 1.000	50169.384 50170.039 50171.143 50171.830	0.031 0.017 -0.066 -0.056	0.009 0.005 -0.015 0.002
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	- 11 23/2 19/2 25/2 21/2	0.100 0.100 0.100 0.100 1.000	50786.288 50786.863 50786.863 50786.863 50788.988	-1.180 -1.567 -0.012 -0.033	0.028 0.087 -0.023 0.033
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	- 11 25/2 23/2 19/2 21/2	2 10 1.000 1.000 1.000 1.000	50858.400 50860.909 50862.154 50864.420	-2.650 -2.348 -0.063 -0.040	0.001 0.038 -0.056 -0.035
12 3 10 27/2 - 21/2 - 25/2 - 23/2 -	- 11 25/2 19/2 23/2 21/2	³ 9 1.000 0.100 1.000 0.100	50900.357 50900.950 50905.033 50905.691	0.058 -0.006 0.055 -0.020	0.049 -0.003 0.048 -0.016
12 3 9 27/2 - 21/2 - 25/2 - 23/2 -	- 11 25/2 19/2 23/2 21/2	3 8 0.100 1.000 0.100 1.000	50900.950 50901.565 50905.691 50906.313	-0.007 -0.051 0.066 -0.047	-0.016 -0.048 0.059 -0.043
12 , 11 27/2 - 25/2 - 21/2 - 23/2 -	- 11 25/2 23/2 19/2 21/2	0.100 0.100 0.100 1.000	51517.502 51517.724 51518.023 51519.258	0.474 0.018 -0.104 0.443	0.012 0.017 0.025 -0.014
13 12 27/2 - 25/2 - 29/2 - 23/2 -	- 13 27/2 25/2 29/2 23/2	³ 0 13 1.000 1.000 1.000 1.000	44441.733 44445.392 44482.980 44486.143	-0.997 -1.927 -0.613 -2.094	0.019 0.001 0.044 0.042
14 1 13 29/2 - 27/2 - 31/2 - 25/2 -	- 14 29/2 27/2 31/2 25/2	1.000 1.000 1.000 1.000 1.000	45314.448 45320.417 45355.799 45361.203	-0.808 0.871 -0.496 0.569	-0.019 -0.062 0.019 0.020
15 1 1 31/2 - 29/2 - 33/2 - 27/2 -	- 15 31/2 29/2 33/2 27/2	5 0 15 1.000 1.000 1.000 1.000	46261.617 46266.069 46303.187 46307.165	-0.690 -0.277 -0.428 -0.533	-0.030 -0.020 -0.007 0.012
16 1 15 33/2 - 31/2 - 35/2 - 29/2 -	- 16 33/2 31/2 35/2 29/2	5 0 16 1.000 1.000 1.000 1.000	47285.651 47289.727 47327.565 47331.196	-0.631 -0.382 -0.372 -0.607	-0.049 -0.033 -0.018 -0.001
17 1 15 35/2 - 33/2 - 37/2 - 31/2 -	- 17 35/2 33/2 37/2 31/2	7 • 17 1.000 1.000 1.000 1.000	48389.145 48392.993 48431.442 48434.850	-0.530 -0.327 -0.299 -0.572	0.009 0.024 0.005 0.036
18 1 17 35/2 - 39/2 - 33/2 -	- 18 35/2 39/2 33/2	3 0 18 1.000 1.000 1.000	49578.252 49617.344 49620.528	~0.292 ~0.243 ~0.582	0.042 0.023 0.029

TABLE II—Continued

Tran F'	sition - F"	Normalised Weight	Observed Frequency	Resid Without X _{ab}	luals With X _{ab}
19 1 1 37/2 41/2 35/2	a - 19 - 37/2 - 41/2 - 35/2	0 19 1.000 1.000 1.000	50848.120 50887.846 50890.884	-0.327 -0.245 -0.627	-0.011 -0.010 0.002
20 1 1 41/2 39/2 43/2 37/2	9 - 20 - 41/2 - 39/2 - 43/2 - 37/2	0 20 1.000 1.000 1.000 1.000	52201.741 52205.209 52245.672 52248.464	-0.566 -0.298 -0.237 -0.677	0.001 -0.002 -0.026 -0.002
21 1 2 41/2	o - 21 - 41/2	⁰ ² 1 0.010	53652.430	-0.186	0.093
14 o 1 29/2 27/2 31/2 25/2	• - 13 - 27/2 - 25/2 - 29/2 - 23/2	1 13 1.000 1.000 1.000 1.000	24966.261 24970.004 24993.737 24999.436	0.964 0.270 0.032 1.343	0.002 -0.017 0.011 0.009
15 ₀ 1 31/2 29/2 33/2 27/2	5 - 14 - 29/2 - 27/2 - 31/2 - 25/2	1.000 1.000 1.000 1.000 1.000	29875.048 29878.788 29902.383 29907.698	0.837 0.545 0.004 1.330	0.030 0.018 -0.011 -0.020
16 o 1 33/2 31/2 35/2 29/2	6 - 15 - 31/2 - 29/2 - 33/2 - 27/2	1.000 0.0 1.000 0.0	34816.506 34823.144 34843.644 34850.568	0.721 3.680 0.025 3.310	0.018 0.305 0.016 0.134
17 o 1 35/2 33/2 37/2 31/2	7 - 16 - 33/2 - 31/2 - 35/2 - 29/2	1.000 1.000 1.000 1.000 1.000	39787.743 39789.729 39814.522 39817.797	0.624 -0.756 -0.014 -0.070	-0.004 0.057 -0.020 -0.017
18 o 1 37/2 35/2 39/2 33/2	8 - 17 - 35/2 - 33/2 - 37/2 - 31/2	1 17 1.000 1.000 1.000 1.000	44785.796 44787.977 44812.050 44815.420	0.611 -0.294 -0.067 0.249	0.038 0.082 -0.071 -0.047
19 0 1 39/2 37/2 41/2 35/2	9 - 18 - 37/2 - 35/2 - 39/2 - 33/2	1 18 1.000 1.000 1.000 1.000 1.000	49807.390 49809.383 49833.206 49836.343	0.544 -0.253 -0.028 0.337	0.013 -0.003 -0.029 -0.025

TABLE II-Continued

with large quadrupole moments, of which Br and I are the most common examples. The off-diagonal constant χ_{ab} must also be large, which requires that the principal quadrupole axes be at an angle of more than $\sim 20^{\circ}$ to the inertial axes. The greater the number of near or semi-near degeneracies of the correct type, the greater will be the precision of the derived constants. We are currently applying the method to iodine isocyanate, INCO, with apparently even greater success than for BrNCO, as well as to other molecules. These results will be reported in due course.

It is somewhat of a pity that more definite internuclear parameters could not be obtained. Further progress could be made if the harmonic force field were known, for then a ground state average (r_z) structure could be obtained. However, in view of the

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Transition F' ~ F"	Normalised ^a Weight	Observed ^b Frequency	Resid Without X _{ab}	luals ^C With X _{ab}
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	³ 1 3 1.000 0.100 1.000 1.000	16590.877 16609.323 16611.856 16624.686	-11.334 -5.455 -0.020 -0.142	-0.006 0.147 -0.016 -0.074
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	4 1 4 1.000 1.000 1.000 1.000	20757.792 20763.937 20764.629 20771.106	0.560 0.389 -0.057 -0.055	0.022 0.028 -0.045 -0.010
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	4 0 4 0.100 0.100 0.100 0.100	21031.080 21031.924 21031.924 21035.953	-9.510 -0.127 0.053 -4.522	-0.034 -0.053 0.035 -0.003
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	4 1 3 1.000 1.000 1.000 1.000	21313.553 21316.760 21319.707 21323.394	0.119 -0.050 -0.011 0.109	-0.012 -0.041 -0.007 -0.004
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	5 1 5 1.000 1.000 1.000 1.000	24910.652 24914.219 24916.049 24919.733	0.191 0.114 -0.009 -0.046	0.018 -0.001 0.005 -0.013
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	5 0 5 0.100 0.100 1.000 1.000	25236.625 25236.625 25247.673 25253.866	-0.169 0.061 5.400 11.392	-0.052 0.046 -0.064 0.044
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	5 , 1.000 1.000 1.000 1.000	25577.458 25580.091 25580.857 25584.055	0.215 -0.039 -0.012 0.203	0.0 -0.025 -0.012 -0.018
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	6 1 6 1.000 1.000 1.000 1.000	29062.671 29064.944 29066.810 29069.148	0.122 0.084 ~0.024 ~0.039	0.035 0.026 -0.009 -0.013
$7 \circ 7 - 15/2$ 17/2 - 15/2 15/2 - 13/2 11/2 - 9/2 13/2 - 11/2	6 ° ° 0.100 0.100 1.000 1.000	29439.508 29439.508 29442.917 29443.243	0.075 -0.202 -0.594 -0.530	0.062 0.003 0.004 -0.003
$\begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$	6 1 5 1.000 1.000 1.000 1.000	29840.398 29842.269 29842.269 29842.269 29845.134	0.436 -0.039 0.004 0.471	-0.004 -0.023 -0.003 -0.012

Measured Rotational Transitions (in MHz) of ⁸¹BrNCO

^a Measurements were weighted according to $1/\sigma^2$, where σ is the uncertainty in the measurements. Unit weight corresponded to an uncertainty of 0.03 MHz.

 b Nitrogen hyperfine splitting has been subtracted from the \underline{b} -types.

 $^{\rm C}$ Observed frequency minus the frequency calculated using the constants in Table I.

Transi F' -	tion F"	Normalise	d Observed Frequency	Res: Without Y.	iduals With y.
·	•			^at	^ab
8 1 e 19/2 - 17/2 - 13/2 - 15/2 -	- 7 17/2 15/2 11/2 13/2	1 7 1.000 1.000 1.000 1.000	33213.759 33215.310 33217.031 33218.628	0.035 0.011 -0.055 -0.058	-0.018 -0.025 -0.040 -0.036
8 ° 8 17/2 - 19/2 - 13/2 - 15/2 -	- 7 15/2 17/2 11/2 13/2	0.100 0.100 1.000 1.000	33640.279 33640.279 33642.755 33643.526	-0.364 -0.043 -0.630 -0.172	0.067 -0.054 -0.018 0.0
8 2 7 19/2 - 13/2 - 17/2 - 15/2 -	- 7 17/2 11/2 15/2 13/2	2 6 1.000 1.000 1.000 1.000	33666.139 33667.381 33672.197 33673.552	0.041 0.0 0.049 0.003	0.013 0.004 0.028 0.010
8 2 6 19/2 - 13/2 - 17/2 - 15/2 -	- 7 17/2 11/2 15/2 13/2	2 5 1.000 1.000 1.000 1.000	33686.085 33687.347 33691.803 33693.217	-0.017 -0.069 -0.019 -0.038	-0.038 -0.066 -0.034 -0.033
8 3 6 13/2 - 19/2 - 15/2 - 17/2 -	- 7 11/2 17/2 13/2 15/2	0.010 0.010 0.010 0.010 0.010	33681.647 33682.607 33695.368 33696.133	0.062 0.078 0.074 0.128	0.065 0.073 0.079 0.125
8 3 5 13/2 - 19/2 - 15/2 - 17/2 -	- 7 11/2 17/2 13/2 15/2	7 3 4 0.010 0.010 0.010 0.010	33681.647 33682.607 33695.368 33696.133	-0.019 -0.002 -0.004 0.050	-0.016 -0.008 0.0 0.048
8 i 7 17/2 - 19/2 - 13/2 - 15/2 -	- 7 15/2 17/2 11/2 13/2	7 1 6 0.100 0.100 0.100 1.000	34103.358 34103.358 34103.581 34103.581 34106.842	0.028 1.599 -0.081 1.578	-0.011 0.141 -0.061 -0.007
9 1 9 21/2 - 19/2 - 15/2 - 17/2 -	- 8 19/2 17/2 13/2 15/2	³ 1 8 1.000 1.000 1.000 1.000	37364.100 37365.212 37366.723 37367.891	0.044 0.019 -0.031 -0.017	0.009 -0.005 -0.015 0.005
9 ° 9 19/2 - 21/2 - 15/2 - 17/2 -	- 8 17/2 19/2 13/2 15/2	³ ⁸ 1.000 1.000 1.000 1.000	37838.013 37839.125 37839.817 37841.727	-1.379 0.098 -1.597 -0.046	0.072 0.087 0.061 0.074
9 1 8 17/2 - 21/2 - 19/2 - 15/2 -	- 8 15/2 19/2 17/2 13/2	5 + 7 1.000 1.000 1.000 1.000	38332.348 38344.933 38363.036 38364.182	-33.029 -17.728 -0.762 -0.038	-0.037 0.059 -0.019 -0.014
10 1 10 23/2 - 21/2 - 17/2 - 19/2 -	- 9 21/2 19/2 15/2 17/2	9, 1.000 1.000 1.000 1.000	41513.589 41514.434 41515.728 41516.617	0.043 0.027 -0.027 -0.010	0.018 0.010 -0.008 0.013
10 0 10 23/2 - 19/2 - 21/2 - 17/2 -	- 1 21/2 17/2 19/2 15/2	9 ° ° ° 1.000 1.000 1.000 1.000 1.000	42035.331 42038.338 42053.495 42070.174	0.005 0.698 17.763 32.937	-0.004 0.005 -0.030 -0.001

TABLE III—Continued

Transition	Normalised	Observed	Resid	uals
F' - F"	Weight	Frequency	Without X _{ab}	With X _{ab}
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	1 0.100	42623.983	0.053	0.084
	0.100	42623.983	0.483	-0.089
	1.000	42635.697	13.060	-0.036
	1.000	42652.089	27.282	0.004
11 1 - 10 25/2 - 23/2 23/2 - 21/2 19/2 - 17/2 21/2 - 19/2	1 10 1.000 1.000 1.000 1.000	45662.225 45662.886 45664.006 45664.697	0.062 0.042 0.003 0.006	0.042 0.030 0.028 0.034
$\begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$	0 10 1.000 1.000 1.000 1.000	46203.181 46216.341 46229.030 46230.414	-27.368 -13.090 0.046 -0.580	-0.041 0.001 0.038 0.026
$\begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$	0.100	46882.334	0.024	0.001
	0.100	46882.589	0.965	0.031
	0.100	46882.589	-0.122	-0.077
	1.000	46884.557	1.151	-0.045
$\begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$	1.000	49809.879	0.017	0.001
	1.000	49810.417	-0.003	-0.013
	1.000	49811.346	-0.070	-0.036
	1.000	49811.887	-0.093	-0.055
$\begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$	0 11 0.100 0.100 0.100 1.000	50419.356 50419.787 50419.787 50421.510	-0.899 0.020 -1.284 -0.047	0.030 0.012 -0.029 0.002
$\begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$	2 10 1.000 1.000 1.000 1.000	50490.169 50492.221 50493.316 50495.218	-2.229 -2.023 -0.064 -0.033	0.004 0.035 -0.059 -0.029
$\begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$	³ ⁹ 1.000	50531.253	0.100	0.094
	0.100	50531.756	0.046	0.048
	1.000	50535.147	0.078	0.073
	0.100	50535.675	-0.005	-0.002
$\begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$	³ 0.100	50531.756	-0.030	-0.036
	1.000	50532.268	-0.076	-0.074
	0.100	50535.675	-0.018	-0.023
	1.000	50536.229	-0.075	-0.073
$\begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$	0.100	51139.918	0.371	0.029
	0.100	51140.147	0.034	0.032
	0.100	51140.415	-0.057	0.027
	1.000	51141.417	0.372	0.025
$\begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$	1.000	53956.629	0.040	0.027
	1.000	53957.085	0.023	0.016
	0.100	53957.794	-0.124	-0.067
	1.000	53958.365	-0.031	0.035
$\begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$	0 13 1.000 1.000 1.000 1.000	44338.710 44341.957 44373.009 44375.878	-0.730 -1.300 -0.447 -1.433	-0.003 -0.009 0.024 0.026

TABLE III—Continued

TABLE III—Continued

Transition F' - F	Normalised Weight	Observed Frequency	Resid Without X _{ab}	uals With X _{ab}
$\begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$	14 0 18 2 1.000 2 1.000 2 1.000 2 1.000	45198.833 45203.962 45233.165 45237.912	-0.535 1.027 -0.359 0.787	0.027 -0.067 0.009 -0.030
15 1 14 - 31/2 - 31/ 29/2 - 29/ 33/2 - 33/ 27/2 - 27/	15 _{0 15} 2 1.000 2 1.000 2 1.000 2 1.000 2 1.000	46132.138 46135.813 46166.698 46170.031	-0.488 -0.171 -0.301 -0.356	-0.021 -0.008 -0.002 0.011
16 , 15 - 33/2 - 33/ 31/2 - 31/ 35/2 - 35/ 29/2 - 29/	16 0 16 2 1.000 2 1.000 2 1.000 2 1.000 2 1.000	47141.155 47144.494 47175.957 47179.023	-0.399 -0.240 -0.253 -0.395	0.011 0.0 -0.002 0.026
$\begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$	17 0 17 2 1.000 2 1.000 2 1.000 2 1.000 2 1.000	48228.193 48231.347 48263.357 48266.234	-0.394 -0.268 -0.222 -0.398	-0.015 -0.023 -0.007 0.025
18 17 - 37/2 - 37/ 35/2 - 35/ 39/2 - 39/ 33/2 - 33/	18 0 18 2 1.000 2 1.000 2 1.000 2 1.000 2 1.000	49395.853 49398.883 49431.438 49434.146	-0.380 -0.248 -0.170 -0.383	-0.015 -0.013 0.018 0.041
20 19 - 41/2 - 41/ 43/2 - 43/ 37/2 - 37/	20 0 20 2 1.000 2 1.000 2 1.000 2 1.000	51983.271 52019.775 52022.159	-0.401 -0.151 -0.447	-0.011 -0.002 0.018
14 o 14 - 27/2 - 25/ 31/2 - 29/ 25/2 - 23/	13 1 13 2 0.100 2 0.100 2 0.100 2 0.100	24515.044 24534.742 24539.294	0.276 -0.024 0.864	0.083 -0.039 -0.074
$\begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$	14 1 14 2 0.100 2 0.100 2 1.000 2 1.000	29382.081 29385.286 29405.051 29409.292	0.538 0.383 0.004 0.915	-0.033 0.041 -0.006 -0.015
$\begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$	15 1 15 2 1.000 2 1.000 2 1.000 2 1.000 2 1.000	34285.015 34289.226 34307.728 34312.549	0.511 1.655 -0.008 1.774	0.014 0.096 -0.015 0.015
17 b 17 - 35/2 - 33/ 33/2 - 31/ 37/2 - 35/ 31/2 - 29/	16 1 15 2 1.000 2 1.000 2 1.000 2 1.000 2 1.000	39217.570 39219.283 39240.010 39242.688	0.447 -0.648 -0.006 -0.111	0.003 -0.001 -0.010 -0.006
$\begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$	17 1 17 2 1.000 2 1.000 2 1.000 2 1.000 2 1.000	44176.871 44178.762 44198.933 44201.684	0.425 -0.260 -0.009 0.189	0.021 0.018 -0.011 -0.007
19 o 19 - 37/2 - 35/ 41/2 - 39/ 35/2 - 33/	18 1 18 2 1.000 2 1.000 2 1.000	49161.623 49181.401 49183.967	-0.136 -0.056 0.177	0.045 -0.057 -0.073

TABLE IV

	I		II	III
r(Br-N)/Å	1.836		1.847	1.863
r(N-C) ^a /A	1.225		1.225	1.225
r(C-O) ^a /Å	1.162		1.162	1.162
<(BrNC)	121.59°		119.44°	116.74°
<(NCO) ^b	0°		4°	9.13°
<(Br-N- <u>a</u>) ^C	28.5°		28.65°	28.8°
Comparison of	r(Br-N) with value	s (in Å) in ot	ther molecule:	8
	BrNCO	1.85		
	CH C(0)NUB+ (15)	1 92		

Structural Parameters of Bromine Isocyanate

BrNCO		1.85
CH ₃ C(O)NHBr	(<u>15</u>)	1.82
C ₆ H ₅ C(O)NHBr	(<u>16</u>)	1.82
BrN(COCH ₂) ₂	(<u>16</u>)	1.84
Sum of single bond radii ((<u>17</u>)	1.84

a Value fixed at that of ClNCO (4), ^b Value fixed in a given structural determination, ^c Angle between the Br-N bond and the <u>a</u>-inertial axis.

facts that the infrared spectrum is only poorly known and partially assigned, and that only limited distortion data are available, it was not felt worthwhile to pursue this avenue at this time.

The measurement of χ_{ab} has allowed us to evaluate the principal values of the Br quadrupole tensor. These are given in Table V. The ratios of the corresponding components for the two isotopes again agree well with the ratio of the Br quadrupole moments. The angle θ_{za} between the z-principal quadrupole axis and the a-inertial axis agrees to within one degree with the angle between the *a*-axis and the Br-Nbond. Within the limitations of the structural calculation this difference is probably not meaningful, and we conclude that the BrN bond is not a bent bond.

TABLE	1
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Principal	Values of the Bromin	e Quadrupole	Coupling Tensor

	⁷⁹ BrnCO	⁸¹ BrNCO	
χ _{2,2} /MHz	893.95(46) ^a	746,41(46)	
X/MHz	-449.70(36)	-375.51(31)	
χ _w /MHz	-444.25(26)	-370,90(26)	
$\Theta_{za}^{j}/deg.^{b}$	27.45(1)	27.42(1)	

Uncertainties are one standard deviation in units of the last significant

 θ_{2a} is the angle between the z-principal quadrupole axis and the z-inertial axis. figures.



FIG. 7. The atoms of BrNCO in its principal inertial axis system following structure II (Table IV).

The similarity of the values of χ_{xx} and χ_{yy} implies that the BrN bond is essentially cylindrical. The double bond character, π , evaluated from (18):

$$\pi = -\frac{2}{3} \frac{\chi_{xx} - \chi_{yy}}{eQq_{\text{Br atom}}}$$
(2)

is minuscule. What is more interesting is the degree of ionic character, i, which can be evaluated using the equations of Townes and Dailey (11). The two most abundant resonance forms are

$$Br^+$$

N=C=O and \bar{N} =C=O
I II

where the contribution of form II (see Fig. 7) is *i*, and that of form I is (1 - i). Form II is shown with the positive pole on Br because $|\chi_{zz}| > |eQq_{Br}|$. The ionic character is obtained from

$$\chi_{zz} = eQq_{\rm Br}[(1-i) + 2i(1+\epsilon)] \tag{3}$$

where the factor $(1 + \epsilon)$ accounts for the decreased screening effect at the Br nucleus by the electrons in form II, and has the value 1.15 (11). In BrNCO, $i \sim 12\%$, a rather greater value than that for Cl in ClNCO, in keeping with the rather lower electronegativity of Br compared to Cl.

ACKNOWLEDGMENT

We thank Thomas Nicol for computing assistance.

Br

RECEIVED: January 27, 1986

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