X-Ray and SCF–MO Model Study of the Complex Formed between *N*-Bromosuccinimide and 1,4-Diazabicyclo[2.2.2]octane

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X-Ray analysis of the structure of the complex (**1**) formed between *N*-bromosuccinimide and the tertiary base 1,4-diazabicyclo[2.2.2]octane (DABCO) shows the compound to contain a nearly linear [175.1(2)°] N–Br–N bond with an exceptionally long bromine to DABCO distance [2.332(4) Å] and a bromine to succinimido distance of 1.945(4) Å; MNDO and *ab initio* SCF-MO calculations on the model system *N*-chlorosuccinimide + NH_3 show charge transfer to occur from both the halogen and the amine to the succinimido moiety upon complex formation.

Although complexes between amines and either halogens (Cl_2 or Br_2)[1] or *N*-halogenosuccinimides[2] have been known for some time, and are found to be very useful oxidation reagents,[1–3] few structural studies of these species have been made.[4] In particular, the structure of the complex formed between *N*-bromosuccinimide (NBS) and the tertiary base 1,4-diazabicyclo[2.2.2]octane (DABCO)[2] is not known and the reasons for its reactivity are not well established.

When benzene solutions of *N*-bromosuccinimide and DABCO are mixed slowly over a period of several hours, crystals of a (2:1) complex (**1**) are obtained. The unit cell contains only two $(NBS)_2$DABCO dimeric units, the DABCO

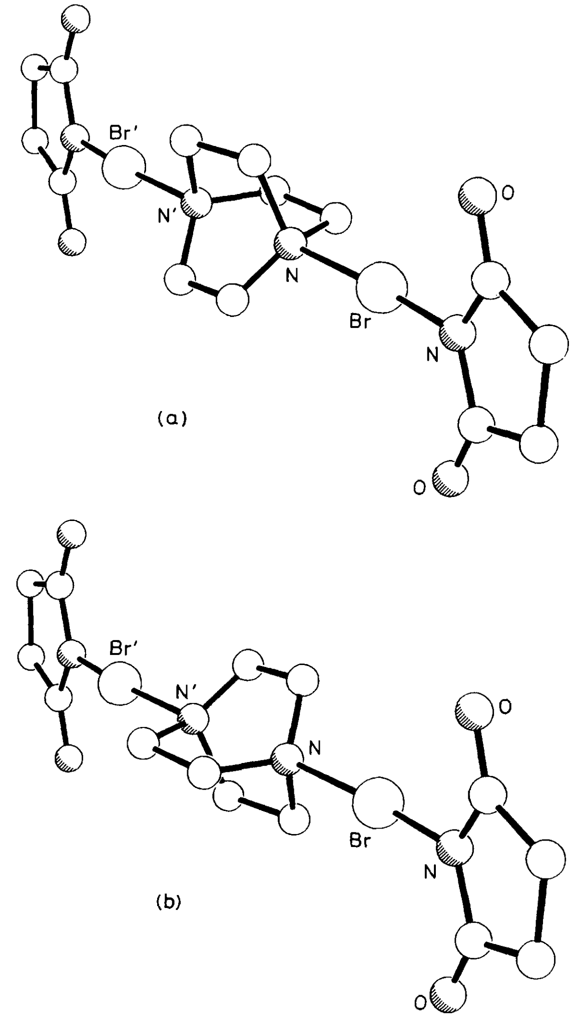

Figure 1. The molecular structure of (**1**) showing the two conformations (a) and (b).

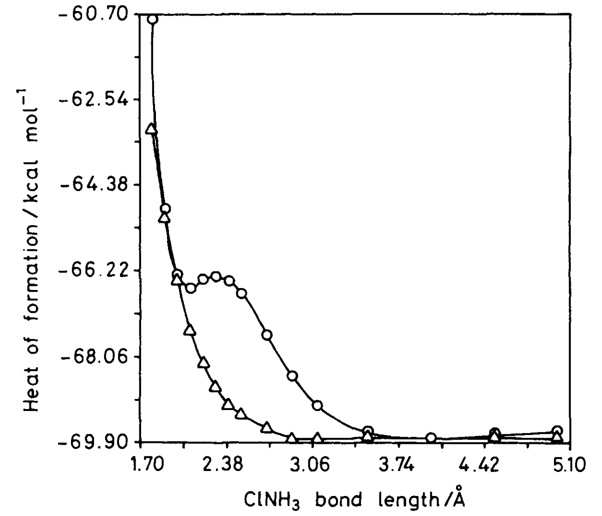

Figure 2. Calculated relative energies (in kcal/mol; 1 cal = 4.184 J) for the interaction of NH_3 and *N*-chlorosuccinimide. ○, MNDO, △, STO 3G.

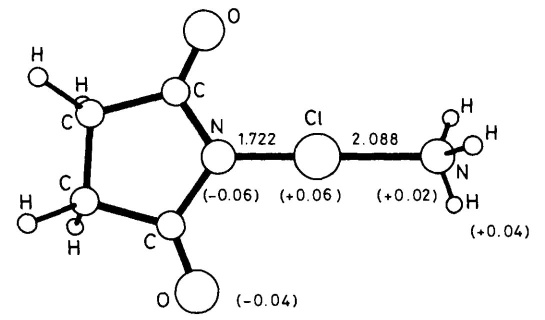

Figure 3. Calculated MNDO structure for the *N*-chlorosuccinimide–NH_3 complex (**2**), showing the calculated change in net atomic charge as a result of complexation.

moiety being disordered about a crystallographic centre of symmetry.† This results in the two conformations shown in Figures 1(a) and (b). The near-linear N–Br–N chain [NBrN angle 175.1(2)°] is found to have exceptionally long bonds to bromine. That to the succinimido moiety is 1.945(4) Å which is significantly longer than other Br–N distances where the nitrogen has sp^2 co-ordination; in *N*-bromobenzamide[5] and *N*-bromosuccinimide[5] for example, the N–Br distance is in the range 1.82—1.84 Å. The bromine–DABCO bond length is 2.332(4) Å which represents the longest N–Br bond yet observed, being considerably longer than other Br–N(sp^3) distances.[5] The average of the two Br–N bond lengths in (**1**) is 2.14 Å, which is in fact very similar to the reported Br–N bond lengths in bis(quinuclidine) bromonium tetrafluoroborate[4a] or bis(quinoline) bromonium perchlorate.[4b]

In order to investigate the bonding in the complex (**1**), we have carried out MNDO[6] and *ab initio*[7] SCF–MO calculations on the model system (**2**), chosen to render the problem computationally feasible.‡ A reaction path calculation using the MNDO method was carried out by varying the Cl–NH_3 bond length from 5.0 to 1.8 Å (Figure 2), all other geometrical variables being fully optimised. *Ab initio* calculations using a STO 3G basis set were carried out at the corresponding MNDO-optimised geometries. A minimum in the MNDO calculated energy was found at a Cl–NH_3 distance of 2.088 Å and a succinimido N–Cl distance of 1.722 Å (Figure 2). The ratio of these distances (1.213) is almost exactly that found in the *X*-ray structure of (**1**). The lack of such a minimum in the *ab initio* potential (Figure 2) is probably an artifact of the minimal basis set used; the use of a larger basis set was precluded by program size limitations. The calculated MNDO electron density distribution shows a transfer of electron density from the NH_3 to the succinimido fragment, with the Cl becoming more positive by 0.06 e in the process (Figure 3).

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† *Crystal Data:* $C_{14}H_{20}Br_2O_4N_4$, monoclinic, a = 9.502(2), b = 9.154(2), c = 10.625(3) Å, β = 105.92(2)°, U = 889 Å^3; space group $P2_1/c$, $Z = 2$, $M_r = 468$, $D_c = 1.75$ g/cm^3, μ(Cu-K_α) = 61 cm^{-1}; 1091 independent observed reflections [$F_0 > 3\sigma(F_0)$, $\theta \leqslant 55°$] were measured on a Nicolet R3m diffractometer with Cu-K_α radiation (graphite monochromator) and using ω scans. The structure was solved by the heavy-atom method and refined anisotropically using absorption-corrected data to give R = 0.053, R_w = 0.061. The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

‡ We were unable to grow suitable crystals of the *N*-chlorosuccinimide–DABCO complex. MNDO parameters for Br have not yet been published and we were accordingly not able to compare directly the calculated and observed structures.

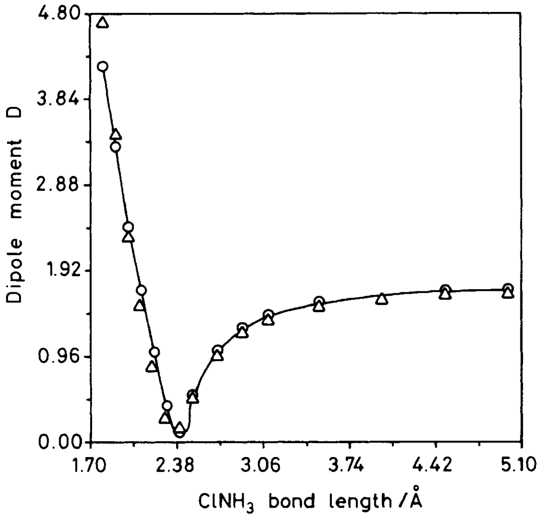

Figure 4. Calculated dipole moments (in Debye) for the *N*-chlorosuccinimide–NH_3 complex (**2**) as a function of N–Cl distance. ○, MNDO; △, STO 3G.

The calculated dipole moment change reflects this charge transfer (Figure 4). The *ab initio* STO 3G dipole moments are essentially superimposable on the MNDO ones, and the change in net atomic charge on the chlorine as calculated from a Mulliken population analysis is also very similar (+0.08 e at an N–Cl distance of 2.1 Å). These calculations suggest that the reactivity of (**1**) as a source of 'Br^+' might be explicable in terms of a transfer of electron density from the halogen to the succinimido fragment upon complexation with DABCO, resulting in a more electrophilic halogen.

Received, 21st November 1983; Com. 1514

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