Crystal and Molecular Structure of 8,12-Diethyl-2,3,7,13,17,18-hexamethylcorrole Hydrobromide

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The crystal structure of the title compound has been determined from *X*-ray data measured on a four-circle diffractometer. The crystals are monoclinic, space group $P2_1/c$, with $a = 13{\cdot}938$, $b = 12{\cdot}882$, $c = 20{\cdot}220$ Å, $\beta = 112{\cdot}87°$, $Z = 4$. 3459 Reflections were measured of which 2492 exceeded $2{\cdot}5\sigma$, and were used in the analysis. The structure was solved by heavy-atom methods and refined by least-squares procedures using large block-diagonal approximations to R 0·063. The macro-ring is not strictly planar; ring A in particular bends out of the mean plane of the ring system: the β-atoms deviate by 0·67—0·69 Å from the plane defined by the four nitrogen atoms. The bromine ion forms three hydrogen bonds with pyrrole nitrogen atoms, N(21), N(22), and N(23), as well as a fourth one with C(39) of a chloroform molecule. A second molecule of chloroform is disordered.

THE present research arose from experiments of Johnson and Kay, designed to synthesize the partly aromatic corrole nucleus as a precursor to the corrin nucleus of vitamin B_{12}.[1-3] The crystal and molecular structure of their original 8,12-diethyl-2,3,7,13,17,18-hexamethylcorrole was reported by Harrison *et al.*[4] and showed that overcrowding occurred between the hydrogen atoms at the centre of the corrole molecule. The present work was undertaken to investigate the geometry of the corrole nucleus when present as a positive ion, fully substituted at all four nitrogen atoms.

EXPERIMENTAL

The crystals were grown by the slow diffusion of light petroleum into a corrole–hydrogen bromide–chloroform solution. Since the air-dried crystals showed only a powder diffraction pattern, all data had to be collected from crystals mounted in contact with their mother liquor in thin-walled Lindemann glass capillaries.

Crystal Data.—$C_{29}H_{35}N_4Br,1{\cdot}5CHCl_3$, $M = 698{\cdot}25$. Monoclinic, $a = 13{\cdot}938$, $b = 12{\cdot}882$, $c = 20{\cdot}220$ Å, $\beta = 112{\cdot}87°$, $U = 3362{\cdot}95$ Å^3, $D_m = 1{\cdot}40$ g cm^{-3}, $Z = 4$, $D_c = 1{\cdot}38$ g cm^{-3}, $F(000) = 1436$. Space group $P2_1/c$ (C^5_{2h}, No. 14). Cu-K_α radiation, $\lambda = 1{\cdot}5418$ Å; μ(Cu-K_α) = 24·7 cm^{-1}.

3459 Independent reflections were measured to a Bragg angle of 55° with Cu-K_α radiation and a scintillation counter on a computer controlled Hilger–Watts four-circle diffractometer. Of these 2492 had integrated intensities greater than $2{\cdot}5\sigma$ and were employed in the analysis. Lorenz and polarization factors were applied and the data were corrected empirically for absorption.[5] The structure was solved by the heavy-atom method and refined initially by isotropic and then by anisotropic least-squares procedures using large block-diagonal approximations to the full normal matrix. The weighting scheme used was an empirical one: $\omega^{-1} = 1{\cdot}0 + [(F_o - P_1)/P_2]^2$ with parameters P_1 and P_2 chosen in such a way as to keep the mean residual constant. All calculations were performed on the Oxford University KDF-9 computer using programmes written by J. S. Rollett, O. J. R. Hodder, and G. Ford.

Initially only the atoms of the corrole nucleus could be placed, but after three rounds of isotropic least-squares refinement a difference electron density synthesis showed the atoms of the first chloroform molecule, C(39), Cl(36), Cl(37), and Cl(38). These were included in the refinement but with C–Cl bond lengths constrained to $1{\cdot}77 \pm 0{\cdot}05$ Å by the method described by Waser.[6] After more refinement further ill defined peaks with heights comparable with those of the chlorine atoms already determined were discovered, close to the centre of symmetry (0, ½, 0) of the unit cell. These were interpreted as a second chloroform molecule which was present in the crystal in a disordered manner but which statistically maintained the centre of symmetry of the unit cell. These atoms were also constrained to the geometry of a chloroform molecule and were refined with an occupancy factor of 0·5. However, since the atomic positions were so ill defined this half molecule was repositioned from difference Fourier syntheses several times in the course of the refinement. Four further cycles of least-squares refinement with all atoms having anisotropic temperature factors reduced R to 0·082 and a difference synthesis showed the positions of 34 of the 36 hydrogen atoms. The final two hydrogen atoms were placed from the difference map obtained after the next round of refinement. The positional parameters of the hydrogen atoms were not refined and the temperature factors were set equal to those of the carbon atoms to which they were attached; by mistake, the temperature factors were allowed to vary in the last least-squares cycles. The changes that occurred are meaningless in relation to thermal motion; they probably reflect inaccuracies in the particular hydrogen atom positional parameters and the anisotropies of the attached carbon atoms. The final R for the statistically significant data was 0·063 and the average shift on all co-ordinates was $< 0{\cdot}5\sigma$.

Figure 1 shows the molecular structure of the diethylhexamethylcorrole monohydrobromide. Final refined positional and thermal parameters with estimated standard deviations of the non-hydrogen atoms are given in Table 1; the unrefined hydrogen atom positional parameters and the thermal parameters used in the last structure factor calculation are recorded in Table 2. Final bond lengths and angles connecting the non-hydrogen atoms are shown

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[2] A. W. Johnson and I. T. Kay, *Proc. Chem. Soc.*, 1964, 89.

[3] A. W. Johnson and I. T. Kay, *Proc. Roy. Soc. A*, 1965, **288**, 334.

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TABLE 1

Atomic co-ordinates (× 10^4), with estimated standard deviations in parentheses

Atom	x/a	y/b	z/c
Br(35)	4128(1)	3356(1)	3201(1)
Cl(36)	1822(4)	1127(3)	2159(2)
Cl(37)	0878(4)	1928(5)	3070(3)
Cl(38)	0969(3)	3176(4)	1939(2)
Cl(20)	−0035(7)	5564(7)	0887(4)
Cl(35)	−0924(7)	4386(8)	−0127(5)
Cl(41)	−0798(7)	4303(9)	−0335(6)
C(39)	1598(9)	2227(10)	2562(7)
C(42)	0326(10)	4833(11)	0301(7)
N(21)	6297(5)	3453(5)	4734(3)
N(22)	4646(6)	2619(6)	4993(4)
N(23)	4662(6)	1020(5)	3959(4)
N(24)	6456(5)	1886(5)	3997(4)
C(1)	7216(6)	3406(6)	4622(4)
C(2)	7942(6)	4037(7)	5135(5)
C(3)	7454(7)	4481(7)	5555(4)
C(4)	6433(6)	4093(6)	5312(4)
C(5)	5666(7)	4152(7)	5597(4)
C(6)	4833(7)	3468(7)	5445(4)
C(7)	4069(7)	3396(7)	5756(4)
C(8)	3482(7)	2531(7)	5496(5)
C(9)	3836(7)	2035(7)	5001(5)
C(10)	3514(7)	1097(8)	4624(5)
C(11)	3893(7)	0589(7)	4172(5)
C(12)	3693(7)	−0427(7)	3884(5)
C(13)	4257(7)	−0606(7)	3475(4)
C(14)	4883(7)	0289(7)	3529(4)
C(15)	5674(7)	0384(7)	3270(4)
C(16)	6416(7)	1207(4)	3469(7)
C(17)	7205(7)	1536(7)	3230(5)
C(18)	7709(7)	2402(7)	3633(4)
C(19)	7220(7)	2627(7)	4119(5)
C(25)	9104(7)	4143(11)	5285(5)
C(26)	7950(10)	5221(9)	6186(6)
C(27)	4028(8)	4138(8)	6335(6)
C(28)	2580(8)	2158(8)	5671(5)
C(29)	1580(9)	2690(10)	5220(8)
C(30)	2975(9)	−1217(8)	4062(7)
C(31)	1879(10)	−1162(13)	3496(7)
C(32)	4269(8)	−1550(7)	3050(5)
C(33)	7435(8)	1004(8)	2646(5)
C(34)	8557(8)	3027(5)	3539(8)

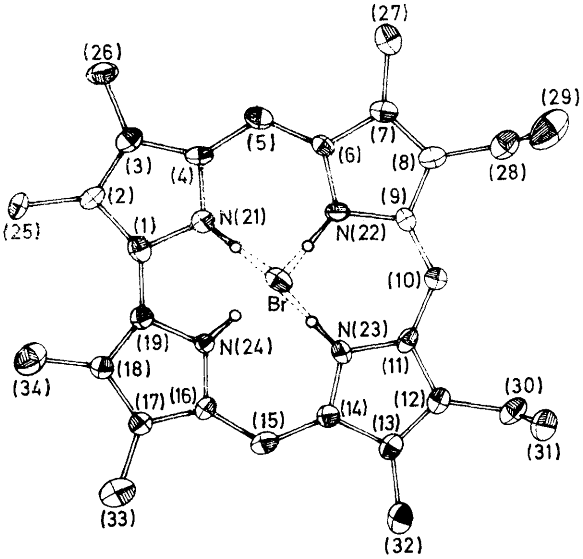

FIGURE 1 Diagram of the molecular structure of the corrole hydrobromide

TABLE 2

Non-refined hydrogen atom co-ordinates (× 10^4)

Atom number	Atom bonded to	x/a	y/b	z/c	B
H(50)	C(25)	8699	4178	5259	10·0
H(51)	C(25)	9050	4500	4875	4·4
H(52)	C(25)	9617	3917	5588	15·0
H(53)	C(26)	7667	4833	5520	24·2
H(54)	C(26)	8550	4667	6605	20·1
H(55)	C(26)	7760	4958	6043	24·7
H(56)	C(5)	5640	4616	5937	1·5
H(57)	C(27)	3483	4683	5113	6·6
H(58)	C(27)	4333	4167	6750	20·5
H(59)	C(27)	3983	3833	6238	5·5
H(60)	C(28)	2667	2167	6205	2·5
H(61)	C(28)	2583	1333	5688	6·7
H(62)	C(29)	1500	3370	5188	7·4
H(63)	C(29)	1983	1472	0854	19·1
H(64)	C(29)	1250	2500	5563	5·6
H(65)	C(10)	2860	0750	4750	2·2
H(66)	C(30)	2920	−1000	4563	4·0
H(67)	C(30)	3450	−2167	4125	15·5
H(68)	C(31)	1333	−1500	3500	11·4
H(69)	C(31)	1717	−1714	2875	21·1
H(70)	C(31)	2583	−0750	3562	21·7
H(71)	C(32)	3917	−2167	3250	9·6
H(72)	C(32)	4950	−1790	3250	4·5
H(73)	C(32)	3583	−1639	2250	5·7
H(74)	C(15)	5667	−0167	2912	16·8
H(75)	C(33)	7917	0417	2750	9·2
H(76)	C(33)	7117	0250	2500	14·9
H(77)	C(33)	7583	1500	2313	8·8
H(78)	C(34)	8650	2750	3063	9·3
H(79)	C(34)	9150	3083	3863	6·5
H(80)	C(34)	8438	3850	3663	12·6
H(81)	N(21)	5633	3453	4290	2·2
H(82)	N(22)	5098	2525	4659	10·3
H(83)	N(23)	4567	1890	3787	7·5
H(84)	N(24)	6138	1661	4348	4·2
H(85)	C(42)	1161	3806	0584	13·6
H(86)	C(39)	2330	2665	2990	17·8

in Figure 2 and Figure 3. Structure factors and U_{ij} parameters are given in Supplementary Publication No. SUP 20981 (15 pp., 1 microfiche).*

RESULTS AND DISCUSSION

As Figures 1—3 show, the bromide ion is situated over the centre of the corrole nucleus, 2·85 Å from the plane of the four inner nitrogen atoms. As expected from the results of ref. 4 on the parent compound, the corrole ring system as a whole does not have a planar conformation. Its characteristics are illustrated by the deviations of the atoms from the calculated least squares plane [7] passing through the four nitrogen atoms recorded in Figure 2 and by Figure 4, which shows a projection of the atomic positions along the plane of the macro-ring. Pyrrole rings B and D are planar within themselves while A and C are slightly folded along a line passing through the two α-carbon atoms; the angle of fold is 1—1·5°. Rings A—C all tilt with their nitrogen atoms towards the bromine ion while ring D alone tilts with N(24) directed away from the ion. The arrangement that occurs appears to be the result of two opposing effects, the opposite charges on the nitrogen and bromide

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* For details of Supplementary Publications see Notice to Authors No. 7 in *J.C.S. Perkin II*, 1972, Index issue.

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ions and possible hydrogen bonding between them, and the overcrowding of the hydrogen and nitrogen atoms in the central part of the molecule.

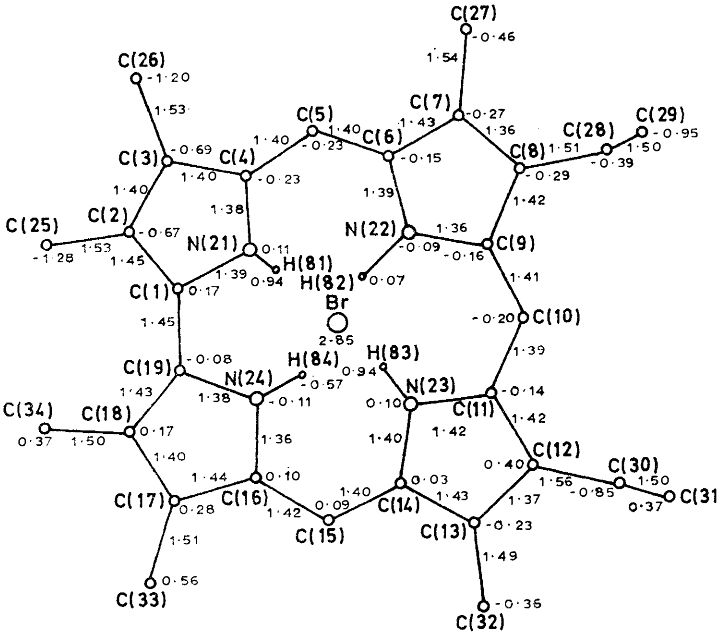

FIGURE 2 Diagram showing the observed bond lengths in the corrole hydrobromide and the distance of each atom from the least squares plane passing through the four nitrogen atoms. E.s.d.s vary from 0·01 to 0·02 Å

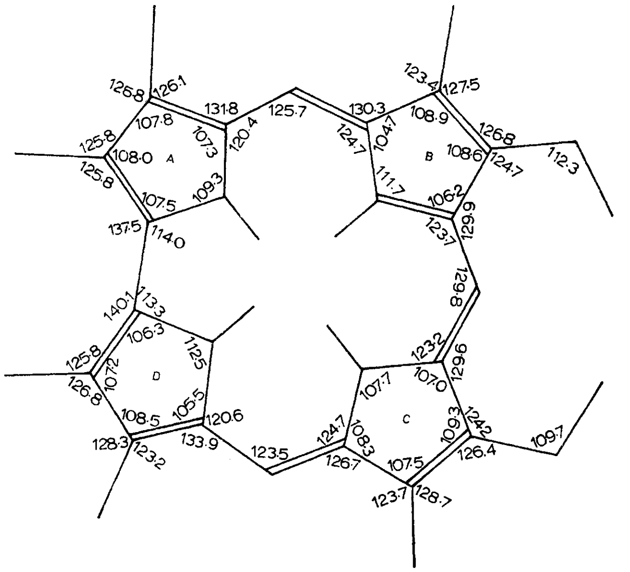

FIGURE 3 Bond angles in the corrole hydrobromide. E.s.d.s vary from 0·7 to 1·0°

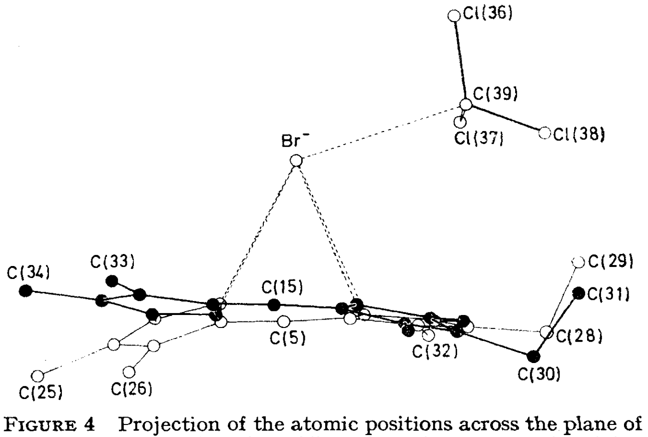

FIGURE 4 Projection of the atomic positions across the plane of the macro-ring. The dotted lines show close contacts involving bromide ion

The overcrowding of the molecule is relieved by small tetrahedral distortions of the nitrogen atoms from their mean plane, shown in Figure 2, accompanied by rather larger distortions of the hydrogen atom positions from this same plane. The A and D rings differ most from one another in tilt, twisting about the C(1)–C(19) direct link between them. Correspondingly, N(21)–N(24) is 2·57 Å, compared with N(21)–N(22), 2·77, N(22)–N(23), 2·94, and N(23)–N(24), 2·71 Å. Though ring D tilts in the opposite direction to the other three rings it is A that makes the most extreme angle to their common plane. There are also suggestive small differences in the bond-length patterns observed in the four rings. In B and C, C_{β}–$C_{\beta'}$ is short, 1·36—1·37 Å, and C_{α}–C_{β} long, 1·42—1·44 Å, as observed commonly in porphyrins (1·34 and 1·45 Å respectively).[8–10] The same pattern appears, but is less marked, in ring D while in ring A all

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the bonds have nearly the same length, 1·39—1·40 Å, throughout. Ring A is therefore most like the *N*-methylated ring found in a copper corrole,[11] which has the C_{β}–$C_{\beta'}$ bond significantly longer than the C_{α}–C_{β} bonds.

The bromide ion forms a pyramid of height 2·85 Å and a distorted square base with the four nitrogen atoms. The distances within it are alternately short, 3·39 and 3·33 Å for Br–N(21) and Br–N(23) respectively, and long, 3·54 for Br–N(22) and 3·55 Å for Br–N(24). Three of the hydrogen atoms may be described as involved in hydrogen bond formation between the nitrogen and bromide ions. Hamilton [12] has suggested, as a criterion for hydrogen bonding, that the distance between the hydrogen atoms and possible acceptors should be at least 0·2 Å shorter than the sum of the covalent radii. This sum may be taken as 3·15 Å for hydrogen and bromine and therefore contacts shorter than 2·95 Å can be considered possible hydrogen bonds. In general such bonds are not linear and the bend may be as high as 30°.[10,13] The data found in our structure, recorded in Table 3, lead to the conclusion that there are two strong hydrogen bonds involving N(21) on ring A and N(23) on ring C, and a third much weaker contact between N(22), H(82), and Br, while the last hydrogen atom H(84) on N(24) of ring D is directed away from the bromide ion, out of contact with it. One further weakly hydrogen-bonded contact can be identified between the bromide ion and the chloroform carbon atom C(39), though the angle here is far from linear. These weak interactions must be treated with caution since the hydrogen atoms cannot be precisely located in the structure in the presence of the heavier atoms. The results obtained do however agree quite well with data found for various other structures containing bromide; the N–H ··· Br distances vary from 3·12 to 3·48 Å.[14-22]

This hydrogen-bonding arrangement probably also accounts for the stabilization of the chloroform molecule, C(39), Cl(36), Cl(37), Cl(38), while the other chloroform molecule, C(42), Cl(20), Cl(35), Cl(41), which is not subjected to such an effect, is disordered. No other unusual short contacts are found in the structure.

TABLE 3

Hydrogen bonding in the corrole hydrobromide

Bond	Length (Å)	Bond	Length (Å)	Shortening (Å)	Angle (°)
N(21)–H(81)	1·01	H(81) ··· Br⁻	2·38	3·16 − 2·38 = 0·78	175
N(22)–H(82)	1·10	H(82) ··· Br⁻	2·93	3·16 − 2·93 = 0·23	115
N(23)–H(83)	1·11	H(83) ··· Br⁻	2·19	3·16 − 2·19 = 0·97	166
C(39)–H(86)	1·19	H(86) ··· Br⁻	2·53	3·16 − 2·53 = 0·63	143
N(24)–H(84)	1·02	H(84) ··· Br⁻	3·59		

Figure 5 shows the projection of the crystal structure down [001].

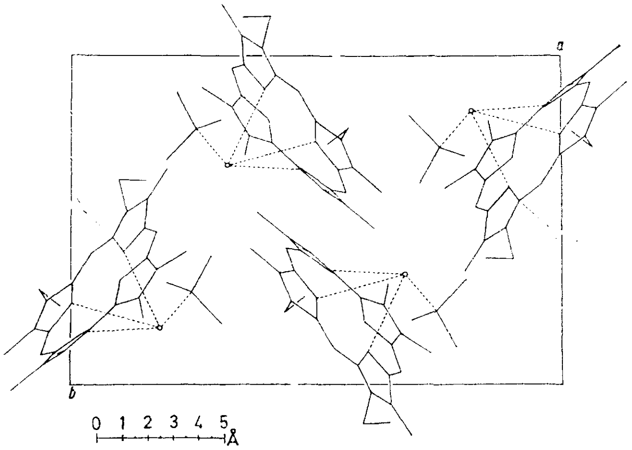

FIGURE 5 The crystal structure of the corrole hydrobromide seen projected along the *c* axis. Dotted lines show possible hydrogen bonded contacts: ○ Br⁻

We thank Professor A. W. Johnson, Sussex, for the sample of the corrole hydrobromide and the Royal Society, London, for financial support (to T. J. B.). Thanks are also due to Dr. E. N. Baker for help during intensity measurements, and Dr. J. S. Rollett for advice.

[2/2527 *Received*, 8*th November*, 1972]

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