N-Methyl-2-bromo-3-(2-indolyl)maleimide–Dioxane

BY I. UEDA

College of General Education, Kyushu University, Ropponmatsu, Chuo-ku, Fukuoka 810, *Japan*

AND S. MIHARA AND T. MATSUO

Department of Organic Synthesis, Faculty of Engineering, Kyushu University, Hakozaki, Higashi-ku, Fukuoka 812, *Japan*

Abstract. $BrC_{13}H_9N_2O_2 \cdot \frac{1}{2}C_4H_8O_2$, monoclinic, $P2_1/c$, $Z = 4$, $a = 5.686$ (2), $b = 16.310$ (9), $c = 15.258$ (5) Å, $\beta = 98.71$ (3)°, $D_m = 1.63$, $D_x = 1.66$ g cm^{-3}. The structure was solved by minimum-function and heavy-atom methods; block-diagonal least-squares refinement led to a final R of 0.052 for 1507 observed reflexions. Molecules in the crystal are involved in van der Waals interactions with each other. The N-methyl-2-bromo-3-(2-indolyl)maleimide molecule is approximately planar. The indole moiety is connected at the 2-position to the maleimide moiety by a C–C partial double bond in an extremely hindered conformation. The molecular structure suggests an intramolecular hydrogen bond and charge-transfer effects from the indole to the maleimide moiety.

Introduction. On photo-irradiation of indole and the 2-bromomaleic anhydride homologue, a single product was obtained. On the basis of spectroscopic evidence, this product was suggested to be a 2-substituted indole (Matsuo, Mihara & Ueda, 1976). However, selective substitution at the 2-position of indole has not previously been reported, in spite of a tremendous amount of work on indole chemistry. Therefore, the present X-ray diffraction study was carried out to obtain conclusive evidence for the suggested structure of the above reaction product.

Deep-red crystals of the title compound were obtained from dioxane solution. Preliminary Weissenberg photographs showed systematic absences indicating space group $P2_1/c$. The unit-cell parameters were obtained by a least-squares procedure using the 2θ values of 15 reflexions measured on a Syntex P1 four-circle diffractometer with Mo $K\alpha$ radiation. The density was measured by flotation in aqueous KI solution. Elemental analyses of the crystals suggested that the unit cell contains two dioxane molecules. A crystal for intensity measurements was manually ground to a sphere of radius 0.203 mm and was coated with paraffin to prevent efflorescence due to evaporation of dioxane. 3936 reflexions within a range of $2\theta \leq 65°$ were collected by the θ–2θ scan technique with a variable scan rate of 4.0 to 24.0° min^{-1} (mono-chromated Mo $K\alpha$ radiation). 1507 independent reflexions with $I > 2.33\sigma(I)$, where σ is the standard deviation, were considered observed and were used for the analysis. Corrections for Lorentz, polarization and absorption effects and for the variation of the monitored intensities were applied.

The structure was solved by a combination of minimum-function and heavy-atom methods. The Br atoms were easily located from the sharpened Patterson synthesis. The positions of all nonhydrogen atoms were obtained from the map of the minimum function and that of the Fourier synthesis phased by the Br atoms. Block-diagonal least-squares refinement of the atomic coordinates and anisotropic thermal parameters reduced R to 0.065. A difference Fourier synthesis calculated at this stage gave the H peaks. Introduction of these H atoms and refinement for all atoms gave the final R of 0.052 for the observed reflexions. Shifts of the positional and thermal parameters of the non-hydrogen atoms were less than one-tenth of their standard deviations. A final difference Fourier synthesis showed no significant features in the undulations, which varied from 0.4 to −0.4 e Å^{-3}, except for some bonding electrons. The final atomic coordinates are listed in Table 1.*

The atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974). Equal weights for the observed reflexions were adopted in the least-squares refinement. All the calculations were performed on the FACOM 230-75 computer in the Computer Centre of Kyushu University with *UNICS* II (Sakurai, Iwasaki, Watanabe, Kobayashi, Bando & Nakamichi, 1974).

Discussion. Fig. 1 shows the crystal structure of a half-cell projected along **a** with the atom-numbering scheme

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Table 1. *Final atomic coordinates and their estimated standard deviations*

	x	y	z		x	y	z
Br	1·0752 (2)	0·4604 (1)	0·7413 (1)	N(2)	1·2614 (11)	0·2207 (4)	0·7500 (4)
C(1)	0·7112 (13)	0·3106 (4)	0·6257 (5)	O(1)	1·4801 (10)	0·3284 (4)	0·8169 (4)
C(2)	0·5951 (14)	0·3824 (4)	0·6021 (5)	O(2)	0·9567 (10)	0·1471 (3)	0·6726 (4)
C(3)	0·3842 (13)	0·3631 (4)	0·5441 (5)	O(3)	0·5183 (10)	0·0759 (3)	0·5418 (4)
C(4)	0·1973 (15)	0·4083 (5)	0·4979 (6)	H(C2)	0·636 (13)	0·433 (4)	0·624 (5)
C(5)	0·0144 (15)	0·3683 (5)	0·4473 (6)	H(C4)	0·196 (13)	0·471 (5)	0·506 (5)
C(6)	0·0098 (14)	0·2832 (5)	0·4404 (6)	H(C5)	−0·121 (14)	0·400 (5)	0·415 (5)
C(7)	0·1933 (14)	0·2368 (5)	0·4832 (5)	H(C6)	−0·130 (15)	0·254 (5)	0·403 (5)
C(8)	0·3795 (13)	0·2768 (4)	0·5350 (5)	H(C7)	0·178 (16)	0·176 (5)	0·481 (6)
C(9)	0·9362 (13)	0·2961 (4)	0·6820 (5)	H(N1)	0·613 (13)	0·193 (5)	0·591 (5)
C(10)	1·0916 (14)	0·3481 (4)	0·7279 (5)	H1(C12)	1·568 (16)	0·163 (5)	0·770 (6)
C(11)	1·3072 (14)	0·3030 (4)	0·7714 (5)	H2(C12)	1·450 (16)	0·155 (6)	0·845 (6)
C(12)	1·4152 (14)	0·1535 (5)	0·7829 (5)	H3(C12)	1·366 (16)	0·102 (6)	0·762 (6)
C(13)	1·0423 (13)	0·2120 (4)	0·6973 (5)	H1(C14)		0·013 (6)	0·543 (6)
C(14)	0·7079 (16)	0·0431 (6)	0·5008 (6)	H2(C14)	0·789 (17)	0·087 (6)	0·474 (6)
C(15)	0·3832 (15)	0·0124 (5)	0·5743 (6)	H1(C15)	0·485 (16)	−0·020 (6)	0·624 (6)
N(1)	0·5798 (11)	0·2463 (3)	0·5848 (4)	H2(C15)	0·236 (16)	0·039 (6)	0·601 (6)
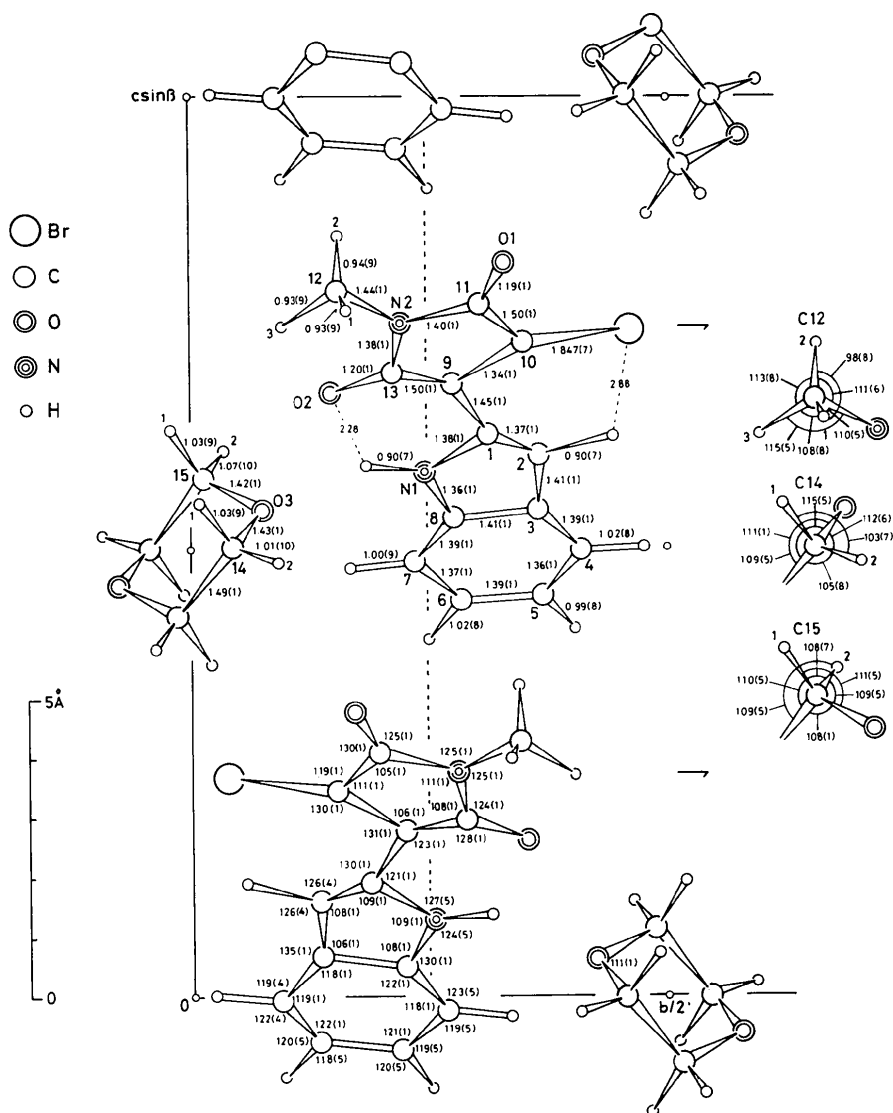
Fig. 1. The molecular arrangement projected down **a**, showing bond lengths (Å) and angles (°) with their e.s.d.'s in parentheses.

and the bond distances and angles. The dioxane and *N*-methyl-2-bromo-3-(2-indolyl)maleimide molecules are involved in rather weak van der Waals interactions with each other. The dioxane molecules evaporate easily and the crystals effloresce at low pressure (15 mm Hg) or at temperatures above 25 °C. The dioxane molecule in the crystal is in a chair conformation and has a centre of symmetry which coincides with a crystallographic centre (at $\frac{1}{2},0,\frac{1}{2}$). The H atoms in the neighbouring methylene groups are in *gauche* positions.

Both the indole and maleimide moieties are planar and are tilted to each other at only 3·7°. There are several characteristic features of the molecular structure. The intramolecular distances Br$\cdots$H(C2) and O(2)$\cdots$H(N1) are 2·88 and 2·28 Å respectively; these are ~0·3 Å shorter than normal van der Waals distances (Pauling, 1960). An intramolecular hydrogen bond between O(2) and H(N1) may be present (this is also supported by the NMR and IR spectra: Matsuo & Mihara, 1977). Although the C(1)—C(9) bond is essentially a single bond which holds the indole and maleimide moieties in a coplanar position, its length

(1·45 Å) indicates partial double-bond character. Intramolecular charge-transfer interactions between the two moieties, as suggested by the electronic spectra, may be partly responsible for the abnormal character of the C(1)—C(9) bond (Matsuo & Mihara, 1977). The bond angles C(10)—C(9)—C(1) and C(9)—C(1)—C(2) are 10° larger than C(13)—C(9)—C(1) and C(9)—C(1)—N(1). In other words, the two moieties are pushed away because of the repulsion between Br and H(C2) at the expense of contractions in the bond angles C(13)—C(9)—C(1) and C(9)—C(1)—N(1). These features have been compared with those in fulvalenes (Ammon & Wheeler, 1975; Ammon, 1976).

Five mesomeric forms are possible (Fig. 2). These mesomeric forms can qualitatively explain the variation of bond lengths in the indole moiety, the linkage part and the maleimide ring. The bond lengths of the indole moiety are in good agreement with those of ervatamine, which has intramolecular charge-transfer effects (Riche, 1974), and tryptamine picrate and D,L-tryptophan picrate–methanol, which have intermolecular charge-transfer effects (Gartland, Freeman & Bugg, 1974). That is, the conjugation character of the mesomeric forms of the indole moieties seems to be common to these compounds. In conclusion, selective substitution at the 2-position of indole is confirmed.
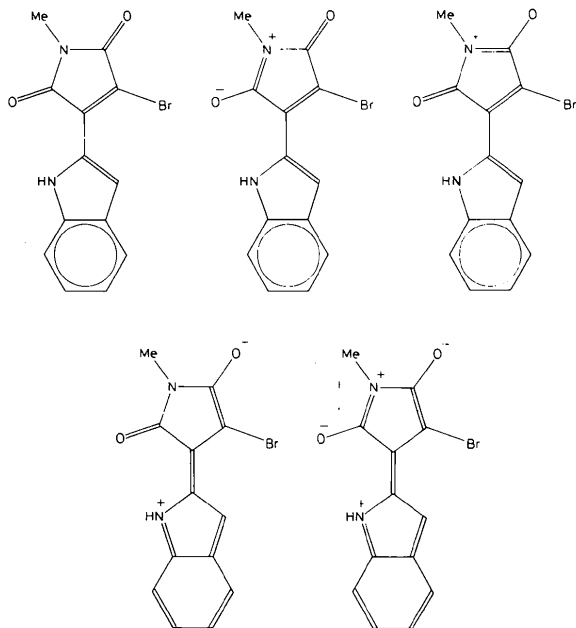
Fig. 2. Possible mesomeric forms considering only O atoms as electron acceptors and N atoms as electron donors.

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