# Structural Aspects and Conformational Analysis of 1,1-Dichloro-2,2-bis[*p*-(*N,N*-dimethylamino)phenyl]ethane

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The crystal and molecular structure of 1,1-dichloro-2,2-bis[*p*-(*N,N*-dimethylamino)phenyl]ethane, a structural analogue of the degradation product of the insecticide DDT, has been determined from three dimensional diffractometric data using Mo-$K_\alpha$ radiation. The compound crystallises in the monoclinic space group $P2_1/c$ with unit cell dimensions $a = 8.091(4)$, $b = 6.145(2)$, $c = 34.384(10)$ Å, $\beta = 91.50(3)°$. The structure was solved by direct methods and refined by full-matrix least-squares analysis to a final $R$ value of 0.075 for 1 522 observed reflections. The ethylenic double bond distance is 1.328(11) Å. The twist about the ethylenic bond is 7.1(5)°. The C–Cl distances are 1.731(9) and 1.743(8) Å. The conformational parameters of this compound are compared with those of other analogous insecticides studied by X-ray diffractometry methods. The conformational angles are low in comparison with the other active insecticides.

DDE [1,1-Dichloro-2,2-bis(*p*-chlorophenyl)ethylene] is a stable primary degradative product of the important wide-spectrum insecticide DDT [1,1,1-trichloro-2,2-bis(*p*-chlorophenyl)ethane]. In the housefly, a dominant gene on chromosome-II controls the production of an enzyme DDT-ase which functions to dehydrochlorinate DDT to the non-insecticidal DDE.[1] However, it is difficult to find fully comparable reported toxicity data; Negherbon[2] refers to the lowest concentration in which certain DDT-related compounds were found toxic to *Anopheles quadrimaculatus* 4th instar. The relevant concentrations were DDT, 0.0025, DDD [1,1-dichloro-2,2-bis(*p*-chlorophenyl)ethane] 0.0025, DDE 1.0, DDA [1,1-bis(*p*-chlorophenyl)acetic acid] 10, and DBP [4,4′-dichlorobenzophenone] 10 ppm. Although these results are only approximate, they give some comparison with DDT. The present compound, a close structural analogue of DDE, was found to be inactive and hence the X-ray crystal structure analysis was undertaken in order to establish some geometrical reasons for such behaviour and to provide additional stereochemical information.

## Experimental

Yellow-tinged crystals were obtained by the slow evaporation of an ethanolic solution of 1,1-dichloro-2,2-bis[*p*-(*N,N*-dimethylamino)phenyl]ethane at room temperature. The crystals were long, thin needles and were found to possess monoclinic symmetry, as determined from oscillation and Weissenberg photographs, with systematic absences $0k0$: $k$ = odd; $h0l$: l = odd, consistent with the space group $P2_1/c$. The cell dimensions and orientation matrix were determined and refined with an automatic Syntex $P2_1$ diffractometer using the least-squares method, from the angular values of 15 reflections. A suitable single crystal of size 0.14 × 0.24 × 0.55 mm was selected for the intensity data collection; the same diffractometer was used with graphite monochromatised Mo-$K_\alpha$ radiation, and the ω-scan technique and a variable scan rate, 2.1–29.3° min$^{-1}$, was used to detect the intensities of all reflections with $3 \leqslant 2\theta \leqslant 53°$. A total of 3 550 unique reflections was measured in the range $h = -11$ to 11, $k = 0$ to 8, and $l = 0$ to 44, of which 1 522 had $I > 1.5\sigma(I)$ and were used for the structure determination and refinement. The intensities were corrected for Lorentz and polarisation factors but no absorption corrections were made. During the data collection one selected reflection was used to monitor the centring and the stability of the crystal and to check for possible variations. No significant change in intensity was observed. Table 1 shows the crystallographic data of the compound.

**Table 1.** Crystallographic data and the experimental parameters for data collection.

| | |
|---|---|
| Molecular formula | $C_{18}H_{20}Cl_2N_2$ |
| Molecular weight ($M_r$) | 335.27 |
| Space group | $P2_1/c$ |
| $a$/Å | 8.091(4) |
| $b$/Å | 6.145(2) |
| $c$/Å | 34.384(10) |
| β/° | 91.50(3) |
| $V_c$/Å$^3$ | 1 709(1) |
| $Z$ | 4 |
| Density (calculated)/g cm$^{-3}$ | 1.303 |
| Density (measured)/g cm$^{-3}$ | 1.310 |
| Radiation (λ) | Mo-$K_\alpha$ (0.7107 Å) |
| μ(Mo-$K_\alpha$)/cm$^{-1}$ | 3.77 |
| Scan type | ω |
| Check reflections | (−1, −1, 8) |
| Data collection range/° | $3 \leqslant 2\theta \leqslant 53$ |
| Number of unique reflections | 3 550 |
| Number of reflections with $I > 1.5\sigma(I)$ | 1 522 |
| Number of variables | 279 |
| $R$ | 0.075 |
| $R_w$ | 0.076 |
| $F$(000) | 704 |
| $T$/K | 297 |

*Structure Determination and Refinement.*—The structure was solved by direct methods using the MULTAN 78[3] program, based on 188 reflections with all $E > 1.5$. The $E$-map corresponding to the solution with the best figure of merit (ABSFOM = 1.180, PSI ZERO = 1.042, RESID = 19.90) revealed all the non-hydrogen atoms of the structure.

Full-matrix least-squares refinement,[4] first using isotropic and then with anisotropic thermal parameters, gave an $R$-value of 0.11. All the hydrogen atoms were located from the difference Fourier synthesis and were included in the isotropic refinement. The refinement was terminated at $R = 0.075$ when all the least-squares shifts were less than the corresponding standard

**Table 2.** Fractional atomic co-ordinates with their estimated standard deviations in parentheses for non-hydrogen atoms.

| Atom | $x$ | $y$ | $z$ |
|---|---|---|---|
| Cl(1) | 0.592 3(3) | 0.144 2(4) | 0.380 8(1) |
| Cl(2) | 0.424 1(3) | −0.016 7(4) | 0.446 7(1) |
| N(1) | 0.219 1(9) | −0.000 1(14) | 0.208 6(2) |
| N(1′) | −0.160 9(8) | −0.595 1(12) | 0.455 3(2) |
| C(1) | 0.240 4(10) | −0.018 2(16) | 0.248 4(2) |
| C(2) | 0.186 4(11) | −0.199 5(16) | 0.268 8(3) |
| C(3) | 0.210 3(11) | −0.216 9(15) | 0.308 7(3) |
| C(4) | 0.285 3(9) | −0.053 3(13) | 0.331 2(2) |
| C(5) | 0.335 0(11) | 0.128 8(16) | 0.311 1(3) |
| C(6) | 0.315 5(11) | 0.144 4(18) | 0.271 1(3) |
| C(7) | 0.302 2(10) | −0.084 6(13) | 0.373 7(2) |
| C(8) | 0.421 3(10) | 0.001 6(14) | 0.396 1(2) |
| C(9) | 0.292 7(17) | 0.178 7(24) | 0.188 6(4) |
| C(10) | 0.126 4(16) | −0.163 0(21) | 0.187 4(3) |
| C(1′) | −0.052 8(10) | −0.482 6(14) | 0.433 3(2) |
| C(2′) | 0.108 5(12) | −0.551 5(16) | 0.427 6(2) |
| C(3′) | 0.220 4(20) | −0.430 5(26) | 0.407 9(4) |
| C(4′) | 0.177 3(10) | −0.223 5(14) | 0.392 5(2) |
| C(5′) | 0.015 6(10) | −0.161 3(15) | 0.395 9(2) |
| C(6′) | −0.097 2(11) | −0.282 4(15) | 0.415 8(2) |
| C(9′) | −0.313 0(13) | −0.500 9(23) | 0.467 3(4) |
| C(10′) | −0.110 9(15) | −0.783 6(19) | 0.477 9(3) |

**Table 3.** Bond distances (Å) with their estimated standard deviations in parentheses.

| Bond | Distance | Bond | Distance |
|---|---|---|---|
| Cl(1)–C(8) | 1.731(9) | C(2′)–C(3′) | 1.365(18) |
| Cl(2)–C(8) | 1.743(8) | C(3′)–C(4′) | 1.418(18) |
| C(7)–C(8) | 1.328(11) | C(4′)–C(5′) | 1.371(12) |
| C(7)–C(4) | 1.477(10) | C(5′)–C(6′) | 1.374(12) |
| C(7)–C(4′) | 1.484(11) | C(6′)–C(1′) | 1.412(12) |
| C(1)–C(2) | 1.393(13) | N(1)–C(1) | 1.379(10) |
| C(2)–C(3) | 1.385(14) | N(1)–C(9) | 1.434(16) |
| C(3)–C(4) | 1.397(12) | N(1)–C(10) | 1.438(14) |
| C(4)–C(5) | 1.381(12) | N(1′)–C(1′) | 1.360(10) |
| C(5)–C(6) | 1.384(14) | N(1′)–C(9′) | 1.430(13) |
| C(6)–C(1) | 1.397(14) | N(1′)–C(10′) | 1.447(13) |
| C(1′)–C(2′) | 1.391(13) | | |

**Table 4.** Bond angles (°) with their estimated standard deviations in parentheses.

| Atom | Angle | Atom | Angle |
|---|---|---|---|
| Cl(1)–C(8)–Cl(2) | 110.3(5) | C(6′)–C(1′)–N(1′) | 121.3(8) |
| Cl(1)–C(8)–C(7) | 126.8(6) | N(1′)–C(1′)–C(2′) | 122.9(8) |
| Cl(2)–C(8)–C(7) | 122.9(6) | C(2′)–C(1′)–C(6′) | 115.7(8) |
| C(4)–C(7)–C(8) | 124.7(7) | C(1′)–C(2′)–C(3′) | 122.8(9) |
| C(8)–C(7)–C(4′) | 118.0(6) | C(2′)–C(3′)–C(4′) | 120.9(1.2) |
| C(4)–C(7)–C(4′) | 117.4(6) | C(3′)–C(4′)–C(7′) | 121.0(9) |
| C(1)–C(6)–C(5) | 122.9(9) | C(5′)–C(4′)–C(7) | 122.6(7) |
| C(4)–C(5)–C(6) | 121.8(9) | C(3′)–C(4′)–C(5′) | 116.4(9) |
| C(3)–C(4)–C(5) | 115.7(8) | C(4′)–C(5′)–C(6′) | 122.6(8) |
| C(5)–C(4)–C(7) | 125.5(7) | C(1′)–C(6′)–C(5′) | 121.3(8) |
| C(3)–C(4)–C(7) | 118.8(7) | C(9)–N(1)–C(1) | 119.7(9) |
| C(2)–C(3)–C(4) | 122.7(8) | C(9)–N(1)–C(10) | 120.5(9) |
| C(1)–C(2)–C(3) | 121.6(8) | C(10)–N(1)–C(1) | 119.8(8) |
| C(2)–C(1)–C(6) | 115.4(8) | C(9′)–N(1′)–C(1′) | 121.7(8) |
| N(1)–C(1)–C(2) | 122.1(8) | C(9′)–N(1′)–C(10′) | 113.6(8) |
| C(6)–C(1)–N(1) | 122.5(9) | C(10′)–N(1′)–C(1′) | 122.1(8) |

**Table 5.** Equations of some least-squares planes and displacement (Å) of the atoms from the planes and some selected torsion angles (°).

| Atom | Deviation/Å | Atom | Deviation/Å |
|---|---|---|---|
| Plane 1: defined by C(1)–C(6); $0.8952X - 0.4281Y - 0.1235Z = 0.5297$ | | | |
| C(1) | 0.005(9) | C(4) | 0.005(8) |
| C(2) | −0.012(9) | C(5) | −0.013(9) |
| C(3) | 0.005(9) | C(6) | 0.007(9) |
| Plane 2: defined by C(1′)–C(6′); $0.2443X + 0.4611Y + 0.8530Z = 11.1141$ | | | |
| C(1′) | −0.023(7) | C(4′) | −0.025(7) |
| C(2′) | 0.019(8) | C(5′) | 0.019(8) |
| C(3′) | 0.028(14) | C(6′) | 0.006(8) |

| Atom | Selected torsion angles/° |
|---|---|
| Plane 3: defined by C(4), C(7), and C(4′); $-0.5768X + 0.8039Y + 0.1447Z = 0.2248$ | |
| C(5′)–C(6′)–C(1′)–C(2′) | −2.62 |
| C(6′)–C(1′)–C(2′)–C(3′) | 2.84 |
| C(3′)–C(4′)–C(5′)–C(6′) | 5.16 |
| C(5′)–C(4′)–C(3′)–C(2′) | −4.88 |
| C(5)–C(6)–C(1)–C(2) | −0.26 |
| C(6)–C(1)–C(2)–C(3) | −1.54 |
| C(3)–C(4)–C(5)–C(6) | −1.73 |
| C(5)–C(4)–C(3)–C(2) | −0.08 |

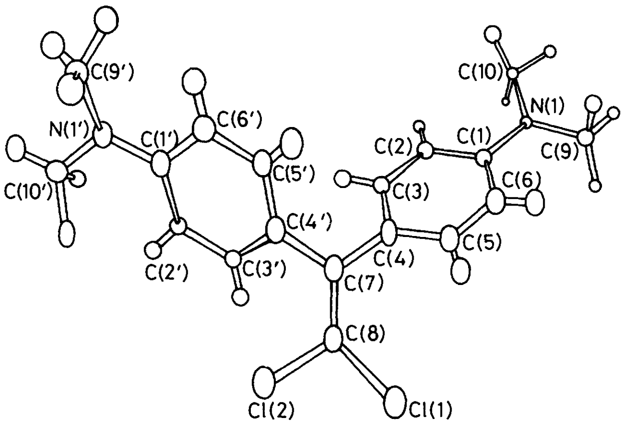

**Figure 1.** Perspective view of the molecule down the *b*-axis with atomic numbering scheme.

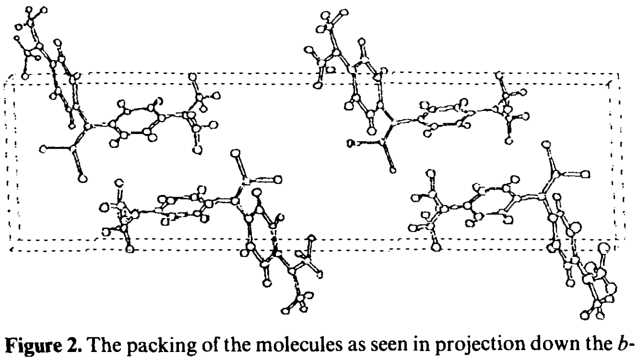

**Figure 2.** The packing of the molecules as seen in projection down the *b*-axis.

**Table 6.** Conformational parameters[a] of DDT-type insecticides.

| Compounds | Activity | $\tau_1$/° | $\tau_2$/° | $\varphi$/° | Ref. |
|---|---|---|---|---|---|
| DDT | Active | 84.2(8) | 47.4(10) | 64.9(4) | 7 |
| DDE | Inactive (molecule 1) | 51.4(4) | 54.5(5) | 81.6(2) | 9 |
| | Inactive (molecule 2) | 78.7(4) | 45.4(2) | 80.2(2) | |
| DDD | Active | 85.4(8) | 74.3(8) | 75.5(3) | 9 |
| DDA | Less active | 85.6(8) | 49.6(4) | 75.5(3) | 16 |
| DBP | Inactive | 27.9(4) | 27.9(1) | 69.1(3) | 16 |
| 2,2-Dichloro-1,1-bis(*p*-chlorophenyl)cyclopropane | Active (molecule 1) | 81.4(5) | 79.9(7) | 69.1(3) | 8 |
| | Active (molecule 2) | 82.2(7) | 79.5(7) | 66.2(3) | |
| Present compound | Inactive | 69.3(1) | 28.4(1) | 85.2(2) | |

[a] See the text for defined angles.

deviations. The function minimized was $\Sigma\omega(|F_o| - |F_c|)^2$ with $\omega = 1/\sigma^2|F_o|$. A final difference Fourier map showed peaks lying in the range −0.28 to 0.32 e Å$^{-3}$. All the molecular geometry, intra- and inter-molecular calculations were performed with the program PARST.[5]

## Results and Discussion

The final atomic positional parameters for the non-hydrogen atoms are listed in Table 2. The thermal parameters for the non-hydrogen atoms and the positional and thermal parameters for the hydrogen atoms have been deposited at the Cambridge Crystallographic Data Centre.* The intramolecular bond lengths and angles are listed in Tables 3 and 4, respectively. Figure 1 represents a perspective diagram of the molecule with the atomic numbering scheme. Some selected least-squares planes and torsion angles are shown in Table 5. Figure 2 shows the molecular packing of the crystal viewed down the *b*-axis. There are no significant intermolecular short contacts.

In discussing the general insecticide model of DDT analogues, and to correlate the biological activity with molecular structure, Rogers *et al.*[6] have suggested that the bulky halogenated group inhibits rotation of the phenyl rings and forces them to take up a 'butterfly' configuration in which the aromatic rings assume nearly coplanar positions. In the present structure, the central carbon atom, C(7), joins the bulky halogenated group ($CCl_2$) to the phenyl rings which take up a 'butterfly' configuration as in DDT.[7]

The C–C bond distances in the benzene rings are in the range expected and agree well with other similar structures.[8–10] The ethylene group appears to shorten the chlorine–carbon distances [1.731(9) and 1.743(8) Å] on the 'C(8)' carbon atoms as observed in the structure of DDE. Similar shortening has also been observed in the *cis* and *trans* isomers of tetrachlorostilbene.[11] The C–C ethylenic bond distance [1.328(11) Å] is slightly longer than the reported value of 1.314(6) Å in unsubstituted ethylene.[12] The twist about this ethylenic double bond has been measured by the angle between the planes through Cl(1), C(8), Cl(2), and C(4), C(7), C(4′). In the present structure the twist angle [7.1(5)°] agrees very well with that of the compound DDE [6.3(4)°] as computed from the published data of Shields.[9] The narrowing of the endocyclic angles at C(1) and C(1′) shows the extensive conjugation between the substituents and the ring in the case of *para*-disubstituted benzene derivatives and exemplified the effect of both $\pi$-donor and $\pi$-acceptor functional groups on the ring geometry.[13] Similar effects have also been observed in *syn-p*-dimethylaminobenzaldehyde oxime[14] and 2-(*p*-dimethylaminophenyl)-4-phenyl-6a-thiathiophthene.[15] The phenyl ring (A) is planar $[\Sigma(D/S)^2 = 5.2]$ but the phenyl ring (B) deviates slightly $[\Sigma(D/S)^2 = 38.2]$ from planarity. The conformation of the phenyl ring (B) is approximately 'boat' with a pseudo mirror along C(1′)–C(4′).

A comparison of the conformational parameters of some insecticide analogues are shown in Table 6; this shows the conformational angles between the planes of C(4), C(7), C(4′) with the phenyl ring [C(1′), C(2′), C(3′), C(4′), C(5′), and C(6′)] ($\tau_1$) and with the phenyl ring [C(1), C(2), C(3), C(4), C(5), and C(6)] ($\tau_2$), and between the two phenyl rings ($\varphi$). The overall stereochemistry is changed with the conformational angles between the plane of C(4), C(7), and C(4′) with both phenyl rings at 69.3(1) and 28.4(1)° and between phenyl groups at 85.2(2)°. It is seen that the conformational angles $\tau_1$ and $\tau_2$ are low and $\varphi$ is high compared with those of DDT, DDD, and 2,2-dichloro-1,1-bis(*p*-chlorophenyl)cyclopropane (Table 6). The effect of low conformational angles or of the ethylenic double bond on the planarity of the part of the molecule or a more subtle effect of overall molecular shape may be responsible for the reduction in activity of the molecule.

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