

Die Ergebnisse thermodynamischer Untersuchungen (Brown & Horowitz, 1955; Brown & Holmes, 1956; Miller & Onyszchuk, 1965; Blackborrow & Lockhart, 1973; Wagner, 1973; Sauer, 1976) zeigen eine Zunahme der Bildungsenthalpien in der Reihenfolge $H_3CCN.BF_3 < C_5H_5N.BF_3 < H_3CCN.BCl_3 < C_5H_5N.BCl_3$.

Unterstellt man einen Zusammenhang zwischen der Bildungsenthalpie der Donor–Akzeptor-Bindung der Addukte mit der Bindungsfestigkeit und dieser weiterhin mit den B–N-Abständen, so sollten die B–N-Distanzen in der Reihenfolge $H_3CCN.BF_3 > C_5H_5N.BF_3 > H_3CCN.BCl_3 > C_5H_5N.BCl_3$ kleiner werden.

Dies ist für die beiden BCl_3 -Verbindungen nicht der Fall und legt den Schluss nahe, dass die Länge der B–N-Bindungen dieser Donor–Akzeptor-Verbindungen in entscheidendem Mass vom sterischen Anspruch der an der Verbindungsbildung beteiligten Moleküle beeinflusst wird und somit der üblicherweise angenommene erwähnte Zusammenhang als zu sehr vereinfacht angesehen werden muss.

Einige intermolekulare F–H-Abstände sind kürzer als die Summe der van der Waals-Radien (2,67 Å; Bondi, 1964) der beteiligten Atome: H(24)–F(11) 2,63 (2), H(13)–F(13) 2,44 (2), H(11)–F(21) 2,57 (2), H(21)–F(23) 2,61 (2) Å. Die Packung der Moleküle sowie die Verkippung der Pyridinringe in der asymmetrischen Einheit gegeneinander wird durch diese F–H-Abstände beeinflusst.

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3-Chlorobiphenyl-4-carbonitrile, $C_{13}H_8ClN$

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Abstract. $M_r = 213.6$, orthorhombic, $Pbca$, $a = 24.05$ (1), $b = 11.41$ (1), $c = 7.70$ (1) Å, $V = 2113.0$ Å³, $Z = 8$, $D_m = 1.32$, $D_x = 1.34$ Mg m⁻³, $Cu K\alpha$, $\lambda = 1.5418$ Å, $\mu = 2.878$ mm⁻¹, $F(000) = 880$, $T = 293$ K, $R = 0.087$ for 1316 observed densitometer and visually measured equi-inclination Weissenberg

data. The average C–C bond in the phenyl rings is 1.383 Å. The molecule is non-planar; the angle between the phenyl rings is 31.0 (3)°; the C–Cl bond is 1.723 (10) Å; the C–C≡N bonds are 1.438 (14) and 1.140 (16) Å, the C–C bond making an angle of 2.5 (5)° with the phenyl plane.

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Table 1. Fractional coordinates ($\times 10^4$) and equivalent isotropic thermal parameters ($\text{\AA}^2 \times 10^3$), with e.s.d.'s in parentheses

$$U_{eq} = (U_{11}U_{22}U_{33})^{1/3}.$$

| | x | y | z | U_{eq} |
|-------|----------|-----------|------------|----------|
| C(1) | 1439 (3) | 3037 (8) | 432 (12) | 39 (4) |
| C(2) | 1310 (4) | 1864 (8) | 588 (13) | 43 (4) |
| C(3) | 799 (4) | 1522 (9) | 1190 (13) | 44 (5) |
| C(4) | 397 (4) | 2350 (10) | 1645 (13) | 48 (5) |
| C(5) | 525 (4) | 3535 (10) | 1453 (14) | 53 (5) |
| C(6) | 1042 (4) | 3862 (9) | 843 (14) | 50 (5) |
| C(7) | 2000 (3) | 3398 (7) | -175 (11) | 37 (4) |
| C(8) | 2462 (3) | 2714 (8) | 228 (12) | 43 (4) |
| C(9) | 2994 (4) | 3053 (8) | -293 (14) | 52 (5) |
| C(10) | 3066 (4) | 4066 (9) | -1203 (15) | 58 (5) |
| C(11) | 2613 (5) | 4746 (9) | -1579 (14) | 54 (5) |
| C(12) | 2082 (4) | 4441 (7) | -1075 (13) | 45 (5) |
| C(13) | -130 (4) | 1985 (11) | 2340 (16) | 64 (6) |
| N | -549 (4) | 1714 (10) | 2902 (18) | 85 (7) |
| Cl | 664 (1) | 46 (2) | 1402 (4) | 65 (1) |

Table 2. Bond lengths (\AA) and bond angles ($^\circ$), with e.s.d.'s in parentheses

| | | | |
|-----------------|------------|-------------------|------------|
| C(1)—C(2) | 1.379 (13) | C(13)—N | 1.140 (16) |
| C(1)—C(6) | 1.378 (13) | C(5)—C(6) | 1.381 (14) |
| C(1)—C(7) | 1.486 (12) | C(7)—C(8) | 1.393 (12) |
| C(2)—C(3) | 1.370 (13) | C(8)—C(9) | 1.396 (13) |
| C(3)—Cl | 1.723 (10) | C(9)—C(10) | 1.363 (15) |
| C(3)—C(4) | 1.397 (14) | C(10)—C(11) | 1.369 (15) |
| C(4)—C(5) | 1.395 (16) | C(11)—C(12) | 1.379 (15) |
| C(4)—C(13) | 1.438 (14) | C(12)—C(7) | 1.391 (12) |
| C(1)—C(2)—C(3) | 120.5 (9) | C(6)—C(1)—C(7) | 120.8 (8) |
| C(2)—C(3)—C(4) | 120.9 (9) | C(2)—C(1)—C(7) | 120.0 (8) |
| C(2)—C(3)—Cl | 118.7 (7) | C(1)—C(7)—C(8) | 119.9 (8) |
| C(4)—C(3)—Cl | 120.5 (8) | C(1)—C(7)—C(12) | 121.5 (8) |
| C(3)—C(4)—C(5) | 118.5 (9) | C(8)—C(7)—C(12) | 118.5 (8) |
| C(3)—C(4)—C(13) | 120.5 (9) | C(7)—C(8)—C(9) | 120.8 (8) |
| C(5)—C(4)—C(13) | 121.0 (10) | C(8)—C(9)—C(10) | 120.0 (9) |
| C(4)—C(13)—N | 178.9 (13) | C(9)—C(10)—C(11) | 119.2 (10) |
| C(4)—C(5)—C(6) | 119.8 (10) | C(10)—C(11)—C(12) | 122.3 (10) |
| C(5)—C(6)—C(1) | 121.2 (9) | C(11)—C(12)—C(7) | 119.2 (9) |
| C(6)—C(1)—C(2) | 119.2 (9) | | |

Introduction. The structure determination of the title compound forms part of an investigation into liquid-crystal compounds and their chemical precursors.

Experimental. D_m measured by flotation in aqueous cadmium *n*-dodecatungstoborate. Pale-yellow transparent crystals, $0.06 \times 0.08 \times 0.27$ and $0.08 \times 0.15 \times 0.15$ mm, respectively, for *c*- and *b*-axis Weissenberg data. 509 reflexions measured by the SERC Microdensitometer Service, Daresbury Laboratory, and 949 by visual estimation from multiple-film photographs using Cu $K\alpha$ radiation. $0 \leq h \leq 30$; $0 \leq k \leq 14$; $0 \leq l \leq 6$. Data merged to give 1316 unique observed reflexions; $R_{int} = 0.06$. Structure solved by Patterson synthesis and refined (on F) by block-diagonal least squares with anisotropic thermal parameters for the non-hydrogen atoms; H-atom positions, initially obtained from a difference synthesis and placed at geometrically reasonable positions, refined with isotropic thermal

parameters; final $R = 0.087$ and $wR = 0.1$, $w = 1/(2|F_{min}| + |F_o| + 2|F_o|^2/|F_{max}| + 5|F_o|^3/|F_{max}|^2)$. $(\Delta/\sigma)_{max}$ in final refinement cycle 0.1 for positional and 0.4 for thermal parameters. Max. and min. heights in final $\Delta\rho$ map +0.45 and -1.43 e \AA^{-3} . Scattering factors from *International Tables for X-ray Crystallography* (1974).

Discussion. Table 1 gives atomic parameters and Table 2 bond lengths and angles.* The atomic numbering is shown in Fig. 1.

The phenyl rings are planar to within $\pm 0.011 \text{ \AA}$, with an average C—C bond of 1.383 \AA . The C(3)—Cl bond, $1.723 (10) \text{ \AA}$, is in good agreement with the value of $1.725 (10) \text{ \AA}$ determined in 2-chlorobiphenyl-4-carboxylic acid (Sutherland & Hoy, 1969*a*). The Cl atom is displaced by $0.010 (6) \text{ \AA}$ from the phenyl ring, C(7) is displaced by $0.046 (9) \text{ \AA}$, C(13) by $0.064 (12) \text{ \AA}$ and N by $0.116 (12) \text{ \AA}$ with the C(13)—C(4) bond being inclined at $2.5 (5)^\circ$ to the phenyl ring. The C(4)—C(13) and C(13)—N bond lengths are $1.438 (14)$ and $1.140 (16) \text{ \AA}$ and angles C(3)—C(4)—C(5), C(3)—C(4)—C(13), C(5)—C(4)—C(13) and C(4)—C(13)—N are $118.5 (9)$, $120.5 (9)$, $121.0 (10)$ and $178.9 (13)^\circ$, respectively; these compare with $1.401 (17)$, $1.137 (19) \text{ \AA}$, $119.2 (10)$, $119.9 (9)$, $120.9 (9)$ and $178.9 (14)^\circ$ for molecule *B* of 4'-bromobiphenyl-4-carbonitrile (Kronebusch, Gleason & Britton, 1976).

The angle between the phenyl rings is $31.0 (3)^\circ$ and, in common with other halogen-substituted biphenyls, the axis of the molecule defined by C(1), C(4), C(7), C(10) deviates significantly from collinearity. Not only is there a rotation ϕ_1 about the central C(1)—C(7) bond but also two other rotations: $\phi_2 = 1.8 (3)^\circ$ of the ring C(1)—(6) about an axis in its

* Lists of structure factors, anisotropic thermal parameters, H-atom parameters, intermolecular distances and the results of mean-plane calculations have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39144 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

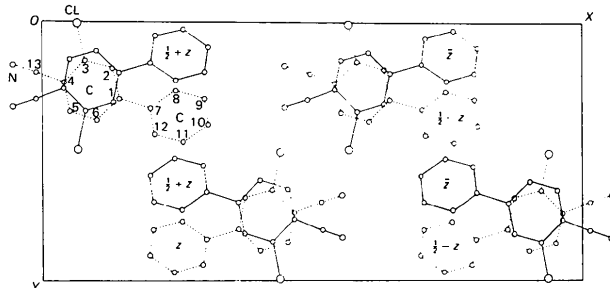


Fig. 1. The arrangement of the molecules in the unit cell viewed along Z.

plane, passing through C(1) perpendicular to C(1)–C(7); and $\varphi_3 = 1.0(4)^\circ$, the corresponding angle of rotation for ring C(7)–(12). A similar value for $\varphi_1 = 30.4^\circ$ has been obtained for 3'-iodobiphenyl-4-carboxylic acid (Sutherland & Mottram, 1972) with corresponding values of 0.7 and 0.4° for φ_2 and φ_3 . φ_1 is significantly smaller than the values of $36.3(6)^\circ$ in 3'-fluorobiphenyl-4-carboxylic acid (Sutherland & Rawas, 1983) and 38.6° in 4-acetyl-3'-bromobiphenyl (Sutherland & Hoy, 1969b). These variations are probably due to intermolecular forces arising from the different packing arrangements in the compounds.

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Garuganin-I,* an Antibiotic, C₂₂H₂₄O₅†

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Abstract. $M_r = 368$, monoclinic, $P2_1/a$, $a = 9.3993(5)$, $b = 15.0431(8)$, $c = 13.7949(8)$ Å, $\beta = 102.577(4)^\circ$, $V = 1903.7$ Å³ at 296 K, $Z = 4$, $D_m = 1.30(1)$, $D_x = 1.285$ g cm⁻³, $\lambda(\text{Mo } K\alpha_1) = 0.70932$ Å, $\mu(\text{Mo } K\alpha) = 0.84$ cm⁻¹, $F(000) = 784$. The structure was refined to a final $R(F) = 0.040$ for 1962 observed reflections. Most of the bond lengths and angles agree with standard values. The structure is stabilized by van der Waals forces.

Introduction. The title compound is an antibiotic obtained from Hindustan Antibiotics Ltd, India. A study of garuganin-I (GRGN), a member of a series of antibiotics, was undertaken to establish a probable structure–activity relationship in this class of antibiotic. Garuganin-I, a plant product, shows anti-asthmatic properties and has a 15-membered macrocyclic ring. Other antibiotics such as rifamycin B (Brufani, Fedeli, Giacomello & Vaciago, 1964) and erythromycin A

(Harris, McGeachin & Mills, 1965) also have large rings, and the conformation of these rings is of interest in establishing the structure–activity relationships.

Experimental. Crystal size $0.3 \times 0.25 \times 0.25$ mm, $\theta/2\theta$ scan with line-profile analysis (Grant & Gabe, 1978), $2\theta_{\text{max}} = 50^\circ$, Picker four-circle automatic diffractometer, graphite-monochromatized Mo $K\alpha$ radiation, no absorption correction, data corrected for direct-beam polarization (Le Page, Gabe & Calvert, 1979) and Lorentz effects, unit-cell parameters determined from least-squares refinement of measured angle values for 48 reflections with $20 < \theta < 25^\circ$. 3366 independent reflections for $2\theta < 50^\circ$ with $-11 < h < 10$, $0 < k < 17$, $0 < l < 16$, 1962 with $I_{\text{net}} > 2.5\sigma(I_{\text{net}})$, 1404 unobserved. Structure solved using *MULTAN* (Germain, Main & Woolfson, 1971), 446 E values > 1.5 for phase generation. Full-matrix least-squares refinement on F ; isotropic temperature factors gave $R(F) = 0.14$; anisotropic refinement gave $R(F) = 0.08$. Hydrogen positions (from ΔF synthesis) and geometry were refined with isotropic temperature factors; final $R(F) = 0.040$, $R_w(F) = 0.028$ with $w = 1/\sigma^2(F_o)$ based on counting statistics; $R(\text{all}) = 0.086$, $R_w(\text{all}) = 0.029$;

* The IUPAC name is 4,6,12-trimethoxy-2-oxatricyclo-[13.2.2.1^{3,7}]jicosa-3,5,7(20),11,15,17,18-heptaen-10-one.

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