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1,6-Interactions between dimethylamino and aldehyde groups in two biphenyl derivatives

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The title compounds, 2-(dimethylamino)biphenyl-2'-carboxaldehyde, C_{18}H_{15}NO, and 2-(dimethylamino)biphenyl-2'6'-dicarboxaldehyde, C_{18}H_{15}NO_2, show similar 1,6-interactions [N···C=O 2.929 (3) to 3.029 (3) Å] between the dimethylamino and aldehyde groups located in the ortho positions of the two rings, which lie at 58.1 (1)–62.4 (1)° to each other.

Comment

Interactions between amino and carboxyl groups in natural products such as (I) and (II) have been interpreted as representing different stages in the progress of the corresponding chemical reaction (Burgi et al., 1973a). Decreasing N···C distances are accompanied by increasing C=O bond lengths. 1,5-N···C interactions between dimethylamino groups and various carbonyl-containing functional groups have been observed in peri-naphthalene systems (Schweizer et al., 1978; Clayden et al., 1999; Hodgson et al., 1999), though the shortest N···C distance observed is only 2.489 (5) Å, for interaction with an aldehyde group in (III). Nevertheless, shorter 1,5-interactions are observed when the electrophilic group is an electron-deficient alkene, as in (IV) [N···C=O 2.413 (2) Å], and almost complete bond formation is observed in (V) [N···C 1.651 (3) Å] (Bell & Wallis, 1999). The use of the N···C distances in such systems as an indicator of the through-space electron-attracting powers of the electrophilic groups has been proposed (O’Leary et al., 2001). In the naphthalene system, the peri groups are constrained to some degree by the bonding geometry of the ring system. We now report the structures of the biphenyls (VI) and (VII), which contain ortho-dimethylamino and ortho-aldehyde substituents on opposite rings such that they are capable of forming 1,6-N···C interactions, but are not compelled by the molecular framework to be near one another at all. The biphenyls were prepared by Suzuki and Stille coupling methodologies and their molecular structures were analysed by single-crystal X-ray diffraction at 150 K.

The results of the crystal structure determinations are shown in Fig. 1, and relevant molecular geometries are summarized in Table 1. Biphenyl (VII) contains two independent molecules in the asymmetric unit. The three molecular conformations of (VI) and (VII) are very similar. The phenyl rings lie at 58.1 (1)–62.4 (1)° to each other such that there is a close N···C contact between the amino N atom and a carbonyl C atom. The dimethylamino group adopts pyramidal geometry, with a N–CH_{3} bond making a torsion angle of 13.2 (3)–15.0 (3)° to the C2–C3 bond of the phenyl ring and directed away from the second phenyl ring. The carbonyl group lies almost in its phenyl-ring plane, with the carbonyl bond directed away from the second phenyl ring. The N···C contact distances, 2.929 (3)–3.029 (3) Å, are longer than in the related naphthalene, (III). The N···C=O angles lie in the range 123.8 (2)–128.2 (2)°, and the theoretical directions of the amino N atom lone pairs lie ca 19–25° to the N···C(=O) vectors. The dimethylamino N atom in (VI) is displaced out of the best plane through its phenyl ring by 0.042 (2) Å towards the carbonyl group, and the carbonyl C atom is displaced out of its phenyl-ring plane by 0.066 Å away from the dimethylamino group. In the two conformations of (VII), the out-of-plane displacements of the corresponding aldehyde C atoms are similar to those in (VI), with values of 0.071 and 0.064 Å, respectively, but the dimethylamino N atoms are not displaced significantly out of the planes of their phenyl groups. Indeed, the Me_{2}N···C bond lengths of 1.402 (3) and 1.410 (3) Å are slightly shorter than in (VI), 1.422 (2) Å. These two effects might be ascribable to the through-bond electron-attracting power of the second carbonyl group, though there are no other significant bond-length changes in the molecular skeletons. The second aldehyde group in (VII) has little effect on the molecular conformation, making only a van der Waals contact with atom H6 on the opposite phenyl ring, with C16···H6 distances of 2.86 (2) and 2.99 (2) Å. There are no particularly short intermolecular interactions in the two crystal structures. In (VI), centrosymmetric C–H···O interactions with graph-set R_{2}^{2}(10) are present [C9···O1(1)]
organic compounds

3.4818 (15) Å and C–H···O' 164.8 (12)°; symmetry code: (i) $1 - x, -y, -z$ and in (VII), chains form comprising C4A/B···O2A/B distances of 3.253 (3) and 3.336 (3) Å, with C–H···O angles of 129 (2) and 159 (3)°, respectively [symmetry code: (ii) $\frac{1}{2} + x, -y, z$ (for A) and $-\frac{1}{2} + x, 1 - y, z$ (for B)].

The observed Me2N···C=O interactions are of similar lengths to the 1,5-Me2N/ketone carbonyl interactions in methadone of 2.911 and 2.912 Å (Bürgi et al., 1973b; By, 1974), where the two groups are not forced to be near one another as they are in the peri-naphthalene series. However, when the 13C NMR spectrum of (VI) was measured in DCI/D2O, the appearance of a new resonance at δ 90.2 indicated addition of the dimethylamino group to a protonated carbonyl group. There are no directly comparable biphenyl structures with 1,6-amino/carbonyl interactions in the Cambridge Structural Database (CSD; Allen & Kennard, 1993). The two molecules of 2,2'-bis(dimethylamino)biphenyl (Staub et al., 1988) adopt conformations with the phenyl rings at 56.1 and 59.0° such that the pyramidal dimethylamino groups are on opposite sides of the molecule. 2-Methoxybiphenyl-$2'$-carboxylic acid (Krygowski et al., 1989) adopts a conformation with the phenyl rings at 54.4 (1)° such that the methoxy O atom lies 3.023 (5) Å from the carboxyl C atom. The methoxy group lies close to the best plane of the phenyl ring, so that the unconjugated lone pair is not well aligned with the MeO···C=O vector. Studies in the naphthalene series have shown that 1,5-MeO···Csp2 interaction distances are remarkably insensitive to the nature of the carbon-containing functional group. In general, biphenyls with one ortho substituent per phenyl ring tend to have their phenyl rings close to perpendicular. Exceptions occur when the substituents are small, as for fluoride or alkyl, e.g. CSD refcode BAWPUK (Jones & Brown, 1982), DECBDP (Neronova, 1968), and NOZZOR and NOZZUX (Ferreira et al., 1998), or can hydrogen bond, as in diols, e.g. JUPTOD (Sartori et al., 1992), NUTSUQ (Byrne et al., 1998), a hydroxy ether JAVHIX (Lin et al., 1989) and the 2,2-diamine DABIPH (Ottersen, 1977), where interplanar angles are ca 40–55°. The structures of (VI) and (VII) are likely to be more reasonable models for intermolecular interactions between dialkyamino groups and aldehydes than the structure of the related naphthalene derivative (III).

**Experimental**

2-(N,N-Dimethylamino)biphenyl-$2'$-carboxaldehyde, (VI): sodium carbonate (6.42 g, 60.6 mmol) dissolved in degassed water (30 ml) was added to a mixture of 2-(N,N-dimethylamino)phenylboronic acid (1.80 g), Pd(PPh3)4 (0.70 g, 0.61 mmol) and 2-bromobenzaldehyde (2.68 g, 14.5 mmol) in a mixture of dry ethanol (5 ml) and 1.2-dimethoxyethane (100 ml) and the mixture heated at reflux for 48 h. The cooled solution was diluted with diethyl ether (200 ml), extracted with 1 M NaOH (50 ml) and then 1 M HCl (4 × 150 ml). The acidic phase was made basic (pH 14) with 6 M NaOH and extracted with ether (3 × 150 ml). The dried (MgSO4) organic solution yielded the crude product which was purified by flash chromatography on silica, eluting first with chloroform followed by ethyl acetate to yield the product as a pale-yellow oil which solidified on standing (1.23 g, 85%), m.p. 348–351 K. 1H NMR (CDCl3): δ 9.57 (1H, s, CHO), 7.92 (1H, d, J = 7.7), 7.65 (1H, t, J = 7.6), 7.47–7.31 (4H, 4H, 7.14 (1H, t, J = 7.4), 7.06 (1H, d, J = 7.2), 2.38 (6H, s, (CH3)2N); 13C NMR (CDCl3): δ 190.7 (C=O), 151.5, 142.7, 133.8, 133.1, 131.1 (x2), 130.0, 129.5, 127.5, 126.7, 125.0, 118.1, 42.2 [(CH3)2N]; νmax (cm$^{-1}$) (KBr): 2832, 1689, 1594, 1492, 1450, 1247, 1193, 945, 770; HRMS (ES): found: 226.1229 (M + H$^+$); C12H12N2O requires: 226.1232 (M + H$^+$).

2-(N,N-Dimethylamino)biphenyl-$2'$-dicarboxaldehyde, (VII): 2-trimethylammonium-N,N-dimethylaniline (0.66 g, 2.35 mmol) and 2-bromoisophthalaldehyde (0.50 g, 2.35 mmol) were refluxed in dry tetrahydrofuran (THF) (25 ml) with Pd(PPh3)4 (0.14 g, 0.12 mmol) and CuI (0.03 g, 0.17 mmol). After 24 h, the amounts of catalysts were doubled and the reaction refluxed for 48 h. The THF was removed on a rotary evaporator, ethyl acetate (50 ml) was added to the residue and the mixture was filtered through Celite. The filtrate was washed...
with water (3 × 30 ml) and brine (30 ml), dried over Na₂SO₄ and evaporated to yield a brown oil. Purification by flash chromatography (SiO₂, 2:1 cyclohexane–diethyl ether) yielded (VII) as a yellow oil which solidified on standing (0.10 g, 17%), m.p. 371–374 K. ¹H NMR (CDCl₃): δ 9.75 (1H, s, CHO), 7.94 (1H, s, CHO), 8.24 (2H, d, J = 7.7), 7.62 (2H, t, J = 7.7), 7.45 (1H, m), 7.15 (3H, m), 2.45 [6H, x, (CH₃)₂N]; ¹³C NMR (CDCl₃): δ 191.2 (C=O), 152.4, 146.2, 133.9, 133.7, 132.6, 130.7, 128.0, 124.9, 122.3, 118.6, 42.5 [(CH₃)₂N]; τmax (cm⁻¹) (KBr): 2859, 1681, 1491, 1456, 1386, 1234, 945, 922, 799, 770; HRMS (ES): found: 254.1178 (M + H)⁺; C₁₅H₁₄N₂O₂ requires: 254.1181 (M + H)⁺.

**Table 1**

<table>
<thead>
<tr>
<th>(VI)</th>
<th>(VIIA)</th>
<th>(VII)</th>
</tr>
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<tr>
<td>N₁–C₁₅</td>
<td>2.9891 (16)</td>
<td>2.929 (3)</td>
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<tr>
<td>N₁–C₁–O₁</td>
<td>126.48 (9)</td>
<td>123.8 (2)</td>
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<tr>
<td>Inter-ring angle</td>
<td>58.94 (6)</td>
<td>59.1 (1)</td>
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<tr>
<td>N₁–C₂</td>
<td>1.4220 (15)</td>
<td>1.402 (3)</td>
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<tr>
<td>Σ bond angles at N₁</td>
<td>341.3 (8)</td>
<td>342.5 (2)</td>
</tr>
<tr>
<td>C₄₁–N₁–C₂–C₃</td>
<td>14.89 (16)</td>
<td>−13.3 (3)</td>
</tr>
<tr>
<td>O₁–C₁–C₈–C₉</td>
<td>6.16 (19)</td>
<td>−10.3 (4)</td>
</tr>
</tbody>
</table>

All H atoms were located in difference Fourier maps and refined with individual isotropic displacement parameters. The C—H bond lengths are 0.947 (16)–1.033 (15) Å in (VI) and 0.92 (3)–1.08 (2) Å in (VII). For compound (VII), reflection data include 1362 merged Friedel pairs (as the absolute structure was not determined).

For both compounds, data collection: DENZO (Otwinowski & Minor, 1997) and COLLECT (Hooft, 1998); cell refinement: DENZO and COLLECT; data reduction: DENZO and COLLECT; program(s) used to solve structure: SHELXL97 (Sheldrick, 1990); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: ORTEPIII (Johnson & Burnett, 1996).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GGI051). Services for accessing these data are described at the back of the journal.

**References**