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Crystal Structure of 2-(*p*-Anilinophenyl)-2-phenylindan-1,3-dione and Its Unexpected Formation

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The title compound, 2-(*p*-anilinophenyl)-2-phenylindan-1,3-dione, was isolated by reacting 2-phenylindan-1,3-dione with *N*,*N*-diphenylhydrazine. This compound crystallizes in the monoclinic crystal system in the space group $P2_1/n$ (#14) with the cell parameters a = 9.837(4)Å, b = 13.221(3)Å, c = 16.325(6)Å, β = 107.914(15)°, Z = 4, and V = 2020.2(12)Å^3. The five-membered ring of the indan-1,3-dione core is slightly bent, forming an envelope-like conformation. The crystal structure is stabilized by the N-H···O=C hydrogen bond with a carbonyl oxygen and by the weak C-H···O=C interaction with another carbonyl oxygen.

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In the course of our study towards the preparation of novel π-expanded nitrogen compounds based on the indan-1,3-dione framework as potential precursors for functional materials,[1-4] we have undertaken the reaction of 2-phenylindan-1,3-dione with *N*,*N*-diphenyl hydrazine. As expected, the condensation product in the enamine form, *i.e.*, 3-(*N*,*N*-diphenylhydrazino)-2-phenyl-1*H*-linden-1-one, was obtained. In addition, an unexpected product, 2-(*p*-anilinophenyl)-2-phenylindan-1,3-dione (**1**), was isolated, and its structure was unambiguously determined by single-crystal X-ray crystallographic analysis. Since large arrays of structural data for indan-1,3-dione derivatives have been surveyed,[5] herein we describe the characterization of the X-ray crystal structure of **1**.

N,*N*-Diphenylhydrazine hydrochloride and 2-phenylindan-1,3-dione in a 1:1 molar *ratio* were refluxed in acetic acid for 2 h. After the usual post-treatment, the reaction mixture was chromatographed on silica gel using dichloromethane as the eluent to afford **1** in 23% yield as yellow prisms of 148°C mp, which exhibited the following spectral and analytical data:

^{1}H NMR ($CDCl_3$); δ 5.77 (1H, broad s), 6.92 (1H, t, J = 7.3 Hz), 6.97 (2H, d, J = 8.8 Hz), 7.04 (2H, d, J = 7.4 Hz), 7.15 (2H, d, J = 8.8 Hz), 7.21-7.33 (7H, m), 7.87 (2H, A_2B_2), 8.07 (2H, A_2B_2). ^{13}C NMR ($CDCl_3$); δ 67.08, 117.04, 118.32, 121.40, 124.06, 127.64, 128.55, 128.77, 129.29, 129.67, 129.77, 136.11, 138.29, 141.60, 142.34, 142.86, 200.02. IR (KBr): 3389, 1738, 1699 cm^{-1}. MS: *m*/*z* 389 (100%), 241 (24%), 165 (23%). *Anal*: Calcd. for $C_{27}H_{19}NO_2$; C, 83.27, H, 4.92, N, 3.60%. Found: C, 83.40, H. 5.02, N, 3.52%. The structure of **1** deduced from these data was confirmed by single-crystal X-ray diffraction analysis.

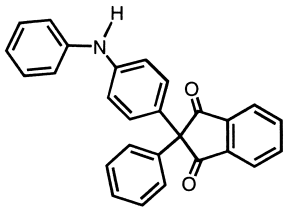

Fig. 1 Chemical structure of **1**.

Single crystals of **1** were isolated by the slow evaporation of an acetonitrile solution of **1**. Their crystal structure was solved by direct methods and refined by full-matrix least-squares procedures to final values of $R1$ = 0.0388. The non-hydrogen atoms were refined anisotropically. All of the hydrogen atoms were found by difference Fourier synthesis and refined isotropically. Figure 1 shows the chemical structure of **1**. Table

Table 1 Crystal parameters and experimental data

Chemical Formula: $C_{27}H_{19}NO_2$	
Formula Weight = 389.14	
T = 93 K	
Crystal System: monoclinic	Space Group: $P2_1/n$ (#14)
a = 9.837(4)Å	
b = 13.221(3)Å	β = 107.914(15)°
c = 16.325(6)Å	
V = 2020.2(12)Å^3	Z = 4
D_x = 1.279 g/cm^3	
Radiation: Mo K_α (λ = 0.71075 Å)	
μ(Mo K_α) = 0.828 cm^{-1}	F_{000} = 840.00
Crystal size = 0.400 × 0.400 × 0.100 mm^3	
Crystal color: yellow	
No. of reflections collected = 4626	
No. of independent reflections = 4090	
$2\theta_{max}$ = 54.9°	
Data/Restraints/Parameters = 4626/0/347	
Goodness-of-fit on F^2 = 1.037	
R indices [$I > 2.00\sigma(I)$)]: $R1$ = 0.0388	
R indices (all data): $R1$ = 0.0438, $wR2$ = 0.1011	
$(\Delta/\sigma)_{max}$ = 0.001	
$(\Delta\rho)_{max}$ = 0.34 e$^-$/Å^3	$(\Delta\rho)_{min}$ = –0.15 e$^-$/Å^3
Measurement: Rigaku RAXIS-RAPID	
Program system: Rigaku Crystal Structure 4.0	
Structure determination: SHELXS-97	
CCDC deposition number: 1028056	

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Table 2 Bond lengths (Å) and bond angles (˚) for non-hydrogen atoms

bond lengths		bond angles	
C1-C2	1.547(2)	C19-N1-C22	128.13(11)
C1-C5	1.547(2)	C1-C2-C3	108.20(10)
C2-C3	1.481(2)	C1-C5-C4	108.49 (10)
C3-C4	1.392(2)	C2-C3-C4	110.12(10)
C4-C5	1.475(1)	C2-C1-C5	102.17 (8)
C1-C16	1.517 (2)	C2-C1-C10	111.56(10)
C1-C10	1.531(1)	C3-C4-C5	110.05(10)
O1-C2	1.208(1)	C5-C1-C16	112.34(10)
O2-C5	1.212(1)	C10-C1-C16	114.51(8)
N1-C19	1.388(1)	O1-C2-C1	125.28(10)
N1-C22	1.404(1)	O2-C5-C1	124.86(9)

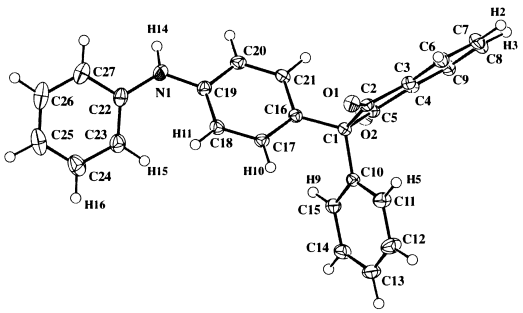

Fig. 2 Molecular structure of **1** with atom labeling scheme. Displacement ellipsoids are drawn at 50% probability. Hydrogen atoms are shown as small spheres of arbitrary radii.

1 gives the crystallographic data and experimental details. The selected bond lengths and angles are given in Table 2. Figure 2 represents an ORTEP diagram of **1** with thermal ellipsoids drawn at 50% probability.

The indan-1,3-dione core adopts an approximately local *Cs* symmetry with respect to the long axis of the structure of **1**. One of the carbonyl groups (C=O2) is involved in intermolecular hydrogen bonding with the amino hydrogen of the neighboring molecule [(N1)H14···O2; 2.17(2)Å, N1···O2; 2.992(2)Å], whereas the other (C=O1) is not involved in hydrogen bonding but participates in an intermolecular short contact between O1···H3(C8) with O1···H3 and O1···C8 distances of 2.58(2)Å and 3.216(2)Å, respectively. Thus, C=O2 [1.212(1)Å] is longer than C=O1 [1.208(1)Å]. The endocyclic angle at C1 of the five-membered ring of the indan-1,3-dione unit, *i.e*., the C2–C1–C5 angle, is 102.17(8)˚, while the angle formed by exocyclic bonds, *i.e*., the C10–C1–C16 angle, is as large as 114.51(8)˚. This is a common feature of the 1,3-indandione framework.[5] The five-membered ring of the indan-1,3-dione unit is not coplanar to its benzene ring, adopting a quite shallow envelope-like conformation by a slight displacement of C1 from the plane toward the phenyl substituent. Thus, the C1–C2–C3–C4 and C1–C5–C4–C3 torsional angles are 5.8(1)˚ and 6.6(1)˚, respectively. Such an envelope-like conformation in the five-membered framework of indan-1,3-dione derivatives is observed in this class of compounds, such as 2-ethyl 2-phenylindan-1,3-dione.[6]

The C1–C2 bond of the indan-1,3-dione framework and the C10–C11 bond of the phenyl ring are close to an eclipsed conformation with a C2–C1–C10–C11 torsional angle of 7. 7(1)˚, which is an unfavorable conformation. On the other hand, the anilino-substituted benzene ring adopts a less unfavorable conformation, showing a corresponding C5–C1–C16–C21 torsional angle of 29.3(1)˚. With respect to the exocyclic C–C bonds connecting the two benzene rings, the C5–C1–C10 angle is 105.23(8)˚, whereas the C2–C1–C10 angle is 111.56(10)˚. The latter is larger than the former, which is ascribed to the steric repulsion due to the eclipsed conformation of C2–C1–C10–C11. The nitrogen atom forms a very small pyramidal structure with a C22–N1–C19 angle of 128.13(1)˚: the sum of the C22–N1–C19, C19–N1–H14, and H14–N1–C22 angle is 358˚. This geometry is almost the same as that of diphenylamines,[7] in which the (Ph)C–N–C(Ph) angle is slightly larger [130.2(2)˚].

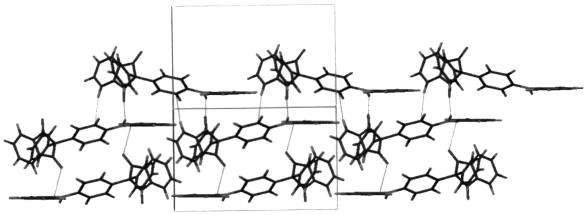

Fig. 3 Packing view of molecules in the unit cell viewed horizontally over the b-axis. Intermolecular NH···O=C hydrogen bonding and CH···π interactions, which form a molecular zigzag chain, are indicated by dotted lines along with the short contacts linking the neighboring chain.

A packing view of the molecules in the unit cell is shown in Fig. 3. The molecules are linked in infinite *zigzag* chains along the *b*-axis by hydrogen bonding between the NH hydrogen and carbonyl oxygen (O2). The N1···O2 distance is 2.999(2)Å. Aside from this intermolecular NH···O hydrogen bonding, the C–H···π short contact is observed on the basis of the (C9) H4···C20 distance of 2.75(2)Å [for C9···C20, 3.712(2)Å] and the arrangement of the H4 pointing almost perpendicularly towards the aromatic ring involving C20. The other carbonyl oxygen (O1) is in short contact with the neighboring molecular zigzag chain at C23 of the *N*-phenyl ring [O1···C23, 3.200(2)Å] (Fig. 3).

The unexpected formation of **1** may involve a condensation reaction accompanied by the release of ammonia from the combined reactants. At this stage, we assume a mechanism involving the nitrenium ion as an intermediate, which could be generated from hydrazines.[8]

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