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Crystal and molecular structure of Michler's ketone as a pure phase

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RESEARCH ARTICLE

ABSTRACT

The pure phase crystals of Michler's ketone, $[4-(CH_3)_2NC_6H_4]_2CO$, are reported herein as monoclinic in the space group $P2_1/c$ with $Z' = 2$ by single-crystal X-ray diffraction. The data collection of the title compound proved quite difficult, which could explain why the structure has not been reported previously. The crystallographically independent molecules in the asymmetric unit differ by dihedral angles of 24.60/30.34° and 25.25/27.20° between the essentially planar 4-dimethylaminophenyl (DMAP) rings and the central $C_2C=O$ plane of the ketone and dihedral angles of 52.14 and 47.41°, respectively, between the DMAP planes. A DMAP ring of each molecule overlaps in the lattice with a methyl ring that overlays the ring centroid of the opposite number (C_{Me}-C_g distances of 3.452 and 3.505 Å), describing sets of trifurcated C_{Ar}-acceptor hydrogen bond interactions (HBIs). The trifurcated HBIs possess H···C_{Ar} distances of 2.90, 2.75, and 2.86 Å; C_{Me}···C_{ar} distances of 3.554(5), 3.798(5) and 3.881(5) Å; and $\angle C_{Me}$-H···C_{Ar} of 115.0, 121.3 and 167.7°, respectively. Stabilization of the asymmetric unit in the title compound is further achieved by supramolecular synthons such as C_{Me}-H···C_{Ar} (2.831 Å), C_{Ar}-H···O (2.561 Å) and C_{Ar}-H···H-C_{Ar} (2.290 Å) and coulombic C_{Me}-O contact (3.209 Å). The structures of the two independent molecules in the asymmetric unit of the title compound were compared with the same molecule as found in the following co-crystals, adducts or salts: a halogen-bonded adduct with 1,4-diiodotetrafluorobenzene; a hydrogen-bonded adduct with a fluorinated phenol; a coordination complex between the ketone and a trimeric mercury acceptor; and two salts from protonation or methylation at one of the amino nitrogen atoms.

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1. Introduction

Michler's ketone ($[4-(CH_3)_2NC_6H_4]_2CO$, **1**, Scheme 1), or *bis*-(4-dimethylaminophenyl)ketone is a popular electron-rich benzophenone whose synthesis was first brought into the limelight in 1876 by Michler [1]. One of its many commercial applications is in the dye industry as a precursor for the preparation of 'crystal violet' and Victoria blue B [2]. Its most important scientific application is as a photosensitizer (PS) for photochemical reactions [3], such as the synthesis of 1,2-divinylcyclobutane from the dimerization of butadiene [4]. A search of the Cambridge Structure Database (CSD version 5.43 update (Jun 2022)) [5] revealed that the molecular structure in the solid state by single crystal X-ray diffraction (SC-XRD) of pure **1** has never been reported. However, several adducts and co-crystals containing **1** have been determined by SC-XRD, namely **2-6** in Scheme 1 [6-9].

Interestingly, each of these derivatives has a different organizational pattern. The adduct **2** with 1,4-diiodo-2,3,5,6-tetrafluorobenzene involves halogen bonding between the carbonyl oxygen and iodine [6]. Co-crystal **3** involves classical hydrogen bonding (H-bonding) between perfluorophenol and carbonyl oxygen [7]. An unusual coordination of ketone oxygen with the trimeric acceptor perfluoro-*ortho*-phenylenemercury (o-C_6F_4Hg)$_3$ is found in the metal complex **4** [8]. This acceptor is

also known to coordinate other ketones [10]. A different way to crystallize **1** was used in compounds **5** and **6**. In compound **5**, the Brønsted basicity of the dimethylaminophenyl group (DMAP) is used by derivatizing with trifluoromethyl sulfonic acid and the SC-XRD of the triflate salt is obtained [7] while in compound **6**, the nitrogen is quaternized with methyl iodide [9]. Herein, we report the single crystal X-ray diffraction structure of **1** and compare its lattice and molecular structures with those of **2-6**.

2. Experimental

2.1. Synthesis of compound 1

A sample of compound **1**, CAS [90-94-8], was prepared by a slight modification of the original report [1] and the crystals were grown from ethanol as small transparent plates with a faint yellow color in the bulk, but the small individual crystals appear to be colourless. The compound's identity and sample purity were determined by SC-XRD. A marginally suitable crystal was selected for data collection after screening many alternatives. The structure solves with $Z' = 2$, further challenging the development of a good refinement model and perhaps explaining why a structure of the pure phase has not been previously reported for this important compound.

Table 1. Selected bond lengths and angles in compounds **1-6**.

Structure	C5-N1 (Å)	C13-N2 (Å)	C1=O1 (Å)	∠C2-C1(O1)-C10 (°)	Reference
1-C1-C17	1.361 (4)	1.359 (4)	1.230 (3)	119.0 (3), 120.4 (3), 120.7 (3)	[This work]
1-C21-C37	1.368 (4)	1.374 (4)	1.234 (3)	120.3 (3), 119.4 (3), 120.3 (3)	[This work]
2	1.352 (6)	1.352 (6)	1.237*	120.1*, 120.1, *119.9*	[6]
3	1.368 (4)	1.371 (3)	1.236 (3)	118.9 (2), 120.3 (2), 120.7 (2)	[7]
4	1.38 (1)	1.381 (1)	1.266 (9)	118.3 (7), 119.9 (7), 121.8 (7)	[8]
5	1.361 (2)	1.476 (2)	1.223 (2)	121.9 (1), 118.0 (1), 120.1 (1)	[7]
6	1.357 (6)	1.496 (5)	1.233 (7)	121.5 (4), 116.8 (4), 121.7 (4)	[9]

* Crystallographic values that lack standard deviations.
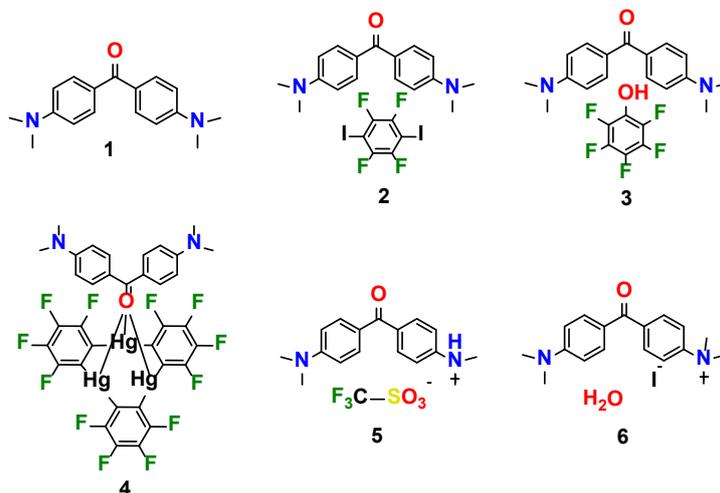
Scheme 1. Line structures of the title compound (**1**) and those of known co-crystals and adducts (**2**-**6**).

2.2. Crystal structure determination

The single crystals of $C_{17}H_{20}N_2O$ (**1**) were grown from the cooling of a hot ethanolic solution. A suitable crystal was selected and mounted in Paratone™ oil using a 100 μm MiTeGen loop on a SuperNova Dual Cu/Mo diffractometer with Pilatus 200K detector. The crystal was kept at 106(9) K during data collection. Using Olex2 [11], the structure was solved with the ShelXT [12] structure solution program using Intrinsic Phasing and refined with the ShelXL [13] refinement package by employing least squares minimization. Crystal and refinement data for compound **1**: Molecular formula: $C_{17}H_{20}N_2O$ (M = 268.35 g/mol), monoclinic, space group $P2_1/c$ (no. 14), a = 30.5246(16) Å, b = 7.4708(2) Å, c = 12.3568(4) Å, β = 90.512(4)°, V = 2817.77(19) Å³, Z = 8, Z' = 2, T = 106(9) K, μ(CuKα) = 0.622 mm⁻¹, D_{calc} = 1.265 g/cm³, 15313 reflections measured (8.69° ≤ 2Θ ≤ 160.632°), 5469 unique (R_{int} = 0.0544, R_σ = 0.0624) which were used in all calculations. The final R_1 was 0.0695 (I > 2σ(I)) and wR_2 was 0.2090 (all data). The completeness of the data was found to be only 94%, which is a consequence of weak diffraction from the very thin plates. All attempts to obtain larger crystals or better data sets have thus far failed. Therefore, the above data set was used to determine the structure of compound **1** reported here. The structural data for this paper have been deposited under CCDC 2184277. Data analysis and visualization were undertaken with Mercury release 2022.2.0 [14].

3. Results and discussions

3.1. Molecular structure description of Michler's ketone in compound 1 and in compounds 2-6

In the structure of compound **1** (Figure 1), its asymmetric unit consists of two crystallographically independent molecules with two dissimilar twists of the DMAP rings. The dihedral angles between the DMAP and the central $C_2C=O$ planes are 24.60/30.34° and 25.25/27.20° while the dihedral angles

between the DMAP planes are 52.41 and 47.41°, in each case describing a 'propellor' twist w.r.t. the central C=O axis of the ketone. Otherwise, there are no statistically significant differences in any interatomic distances or angles at the 99% confidence level.

The C=O bond lengths for the two independent molecules of **1**, and those in the comparison structures **2-3** and **5**, **6** can be averaged to 1.232(5) Å (Table 1). This average fits, at the 99% confidence level, with the standard value reported in reference [15], derived from all data in the 1985 version of the CSD. The C_{Ar}-N(CH₃)₂ distances average to 1.366(6) Å, which is within range of the standard value of 1.371(16) Å at the 99% confidence level [15]. The dimethylamino (DMA) groups are effectively planar with sums of angles in each of the four independent moieties of 360(1)°. The strong DMA donation is also observed by long [1.408(7) Å for bonds from the substituent attachment points] - short [1.374(5) Å for ring-edge bonds] bond alternation in the aromatic rings.

The interatomic distances and angles obtained for compound **1** are generally in good agreement with the earlier values as obtained in derivatives and co-crystal SC-XRD structures of compounds **2-6**. The dihedral angles between the DMAP and the central $C_2C=O$ planes are 27.11/27.11° for compound **2**, 19.02/36.44° for compound **3**, 7.99/51.25° for compound **4**, 19.44/40.37° for compound **5** and 16.95/38.17° for compound **6** while the dihedral angles between the DMAP planes are 49.59° for compound **2**, 52.13° for compound **3**, 57.64° for compound **4**, 55.65° for compound **5** and 51.94° for compound **6**. The noteworthy exception occurs for compound **4** where one of the rings is almost co-planar with the central ketonic moiety. The dimethylamino planes are all effectively planar except for the protonated N in compound **5** and the quaternized N in compound **6**; the two aromatic rings attached to these *pseudo*-tetrahedral aminium and quaternized groups respectively also do not show the long/short bond alternation of the neutral DMA group substitutions, with all the ring C-C bonds corresponding to standard aromatic bond lengths of 1.384(13) Å [15] at the 99% confidence level.

Table 2. Important structure supporting non-classical H-bonds and intermolecular contacts in compound **1** [a].

Atom 1	Atom 2	Length	Length – Σr (vdW)	Symmetry code [b]
C17$_{Me}$	C$_{centroid}$ [c]	3.453	-	*x, y, z*
C29$_{Me}$	C$_{centroid}$ [d]	3.505	-	*x, y, z*
C9$_{Me}$	C$_{centroid}$ [e]	3.479	-	1-*x*, 1-*y*, 2-*z*
C$_{centroid}$ [f]	C30-35$_{plane}$	3.496	-	-*x*, -*y*, 2-*z*
H12	H17C	2.195	-0.205	*x*, 1.5-*y*, -1/2+*z*
H27	O21	2.561	-0.159	*x*, 1/2-*y*, -1/2+*z*
H17A	C23	2.746	-0.154	*x, y, z*
H37A	H32	2.290	-0.110	*x*, 1/2-*y*, -1/2+*z*
C4	H9C	2.831	-0.069	1-*x*, 1-*y*, 2-*z*
H3	C5	2.849	-0.051	1-*x*, -1/2+*y*, 1.5-*z*
H17A	C24	2.856	-0.044	*x, y, z*
O21	C37	3.209	-0.011	-*x*, -*y*, 2-*z*
H17A	C22	2.898	-0.002	*x, y, z*

[a] Atomic contacts shorter than 0.01 Å less than sums of the van der Waals radii of atoms in contact.
[b] Symmetry operations of atoms 2 within the context of contact definition.
[c] Centroid defined by C22/C26/C27/C22/C23/C24.
[d] Centroid defined by C10/C11/C12/C13/C14/C15.
[e] Centroid defined by C2/C3/C4/C5/C6/C7.
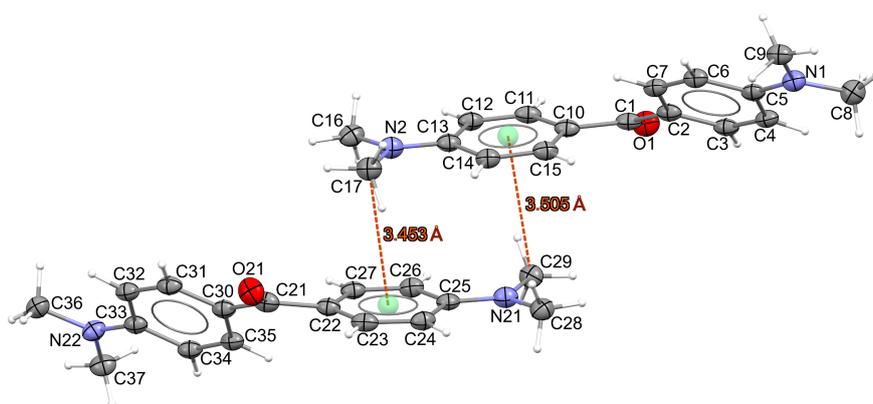[f] Centroid defined by C30/C31/C32/C33/C34/C35.

Figure 1. Displacement ellipsoid (40%) plot showing the asymmetric unit in the structure of **1** with the atom labelling scheme and short C$_{Me}$···C_g (centroid) contacts.

The C-N bond lengths in the structures of compounds **2-6** align with those of the title compound except for those of compounds **5** and **6** which are much longer than the 1.35-1.37 Å reported for compound **1**, also consistent with the loss of strong donation of the N lone pair into the aromatic π-system. The C=O bond lengths agree closely with those of compound **1** except for that of compound **4** which is longer than the two values determined in compound **1** at the 99% confidence level; we attribute this to the bond elongation caused by strong donation to the Hg ions in this coordination complex. The entire set of C=O bond angles agree well with those of compound **1** and all sum to 360(1)°, consistent with rigorous planarity.

3.2. Lattice structural description and short intermolecular contacts

The lattice structure of compound **1** consists of several important intermolecular interactions that are either short contacts or nonclassical hydrogen bond interactions with distances shorter than the sum of the van der Waals radii of the atoms in contact by 0.01 Å or more (Figure 2 and Table 2). The two crystallographically independent molecules of **1** have a DMAP ring overlaying with a methyl ring of the opposite number with C$_{Me}$-C_g distances of 3.452 and 3.505 Å (Figure 1) for which the shortest static contacts are sets of trifurcated C$_{Ar}$-acceptor, hydrogen bond interactions (HBIs) with H···C$_{Ar}$ distances of 2.90, 2.75, and 2.86 Å, C$_{Me}$···C$_{Ar}$ distances of 3.554(5), 3.798(5), and 3.881(5) Å and ∠C$_{Me}$-H···C$_{Ar}$ of 115.0, 121.3, and 167.7°, respectively. A similar type of contacts (pairs of) links the two asymmetric units centrosymmetrically with respect to 1̄ at (½ ½ 1) for which the shortest static contact is C4···H9C. This tetrad of molecules of **1** shown in the packing

diagram (Figure 2) is further linked via a more classic kind of π-stacking involving C30-35 rings centrosymetrically w.r.t. 1̄ at (0 0 1) for which the shortest contact is O21···C37 and the centroid-plane perpendicular distance is 3.496 Å. These contacts, undoubtedly defined primarily by dispersion forces, form the molecules into ribbons approximately parallel to the *c* axis as shown in Figure 2, with a close range of interplanar spacing ranging from 3.453-3.505 Å. These distances are extremely similar to a large number of interplanar π-stacking distances, based on the perpendicular interplanar or centroid-planar separations, in recently reported molecular crystals, that range from 3.335(3) to 3.578(3) Å [16].

The shortest intermolecular contacts are the H-bonds between C$_{Me}$-H27C···H12-C$_{Ar}$, C$_{Me}$-H37A···H32-C$_{Ar}$ and H27···O21. These form links between the ribbons described above and are depicted in Figure 3 as contacts between the normal- and false-coloured orange atoms.

A perusal of the lattice structures of the various adducts, co-crystals, and salts containing compound **1** in structures **2-6** shows that the dominant dispersion-induced contacts, i.e. the interplanar spacings that form the ribbons in Figures 2 and 3, are absent. These self-contacts are replaced by the dominant new contacts that generate these mixed-component lattices. In compound **2**, these involve iodine to oxygen and some C-H (ketone) to C$_{Ar}$ (fluorobenzene) contacts [6]. In compound **3**, the fluorophenol to ketone O contacts are dominant with further contacts from DMA H atoms to some ring fluorine atoms [7]. In compound **4**, there are very few contacts between the coordination complexes, those that dominate are again C-H to ring fluorine atoms [8]. Naturally, in compound **5**, the strongest contacts are from cations to anions, involving protonated DMA with triflate anion oxygen donors [7].
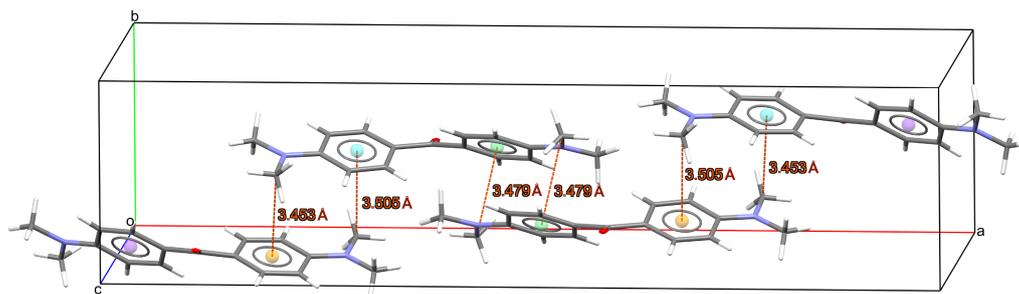
Figure 2. Ribbon-forming C_{Me}-C_g short contacts within (left/right) and between (centre) two asymmetric units in the unit cell of the structure of compound **1**.
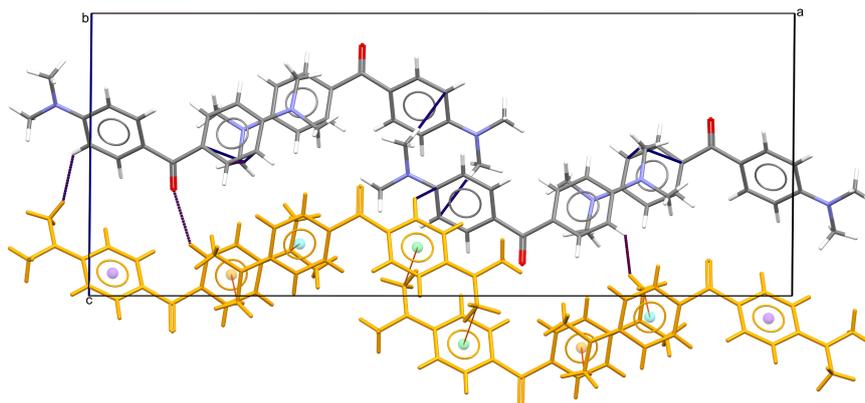

Figure 3. Unit cell packing diagram for compound **1** viewed down the crystallographic *b* axis. The false-colored orange ribbon is that shown in Figure 2. The glide-related second ribbon in normal colors is linked via the strongest intermolecular non-classical H-bonds to the orange-coloured one.

Many additional contacts develop as might be expected for the enhanced lattice energy that develops in a salt. By contrast to compound **1**, the structure of **6** is dominated by chains of classical H-bonds between iodide anions and the waters of solvation and there are a few contacts with the charged ketone exist [9].

4. Conclusions

This work focuses on the report of the first crystal structure of Michler's ketone (**1**), a well-known electron-rich benzo-phenone. Its crystal structure in the space group $P2_1/c$ has a Z' = 2, so that the asymmetric unit consists of two very similar but crystallographically independent molecules with different dihedral angles between the essentially planar, 4-dimethyl-aminophenyl rings and the central C_2C=O planes of the ketone and between the DMAP planes. These molecules are connected via the offset overlay of the dimethylaminophenyl ring of one molecule over the other, such that the methyl to centroid distances are measured to be 3.452 and 3.505 Å. Similar methyl-to-plane and interplanar contacts, dominated by dispersion forces, link the molecules into infinite ribbons. Parallel ribbons are associated in the lattice via additional supramolecular synthons comprising non-classical HBIs. These rather weak contacts are easily displaced in five different known structures of co-crystals, adducts, and salts containing Michler's ketone, which presumably form instead of the pure phase by virtue of the dominating new intermolecular synthons.

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Supporting information ⓢ

Disclosure statement ⒹⓈ

Conflict of interest: The authors declare no conflict of interest.
Author contributions: Ibukun Oluwaseun Shotonwa carried out data analysis and wrote the paper; René T. Boeré solved and refined the crystal structure model as well as reviewing and editing the paper.
Ethical approval: All ethical guidelines have been strictly adhered to.
Sample availability: Samples are not available.

CRediT authorship contribution statement ⒸⓇ

Conceptualization: Ibukun Oluwaseun Shotonwa; Methodology: René T. Boeré; Validation: Ibukun Oluwaseun Shotonwa; Writing - Original Draft: Ibukun Oluwaseun Shotonwa; Writing - Review and Editing: Ibukun Oluwaseun Shotonwa, René T. Boeré.

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