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CRYSTAL STRUCTURE OF 4-HYDROXY-6-METHYL-3-[(1*E*)-1-(2-PHENYLHYDRAZINYLIDENE)ETHYL]-2*H*-PYRAN-2-ONE

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A Schiff base, 4-hydroxy-6-methyl-3-[(1*E*)-1-(2-phenylhydrazinylidene)ethyl]-2*H*-pyran-2-one, is synthesized and characterized by ^{1}H and ^{13}C NMR, IR spectroscopy, ESI-mass spectrometry and single crystal X-ray diffraction analysis. There are three crystallographically independent molecules in the asymmetric unit, space group *C*2/*c*, *a* = 30.011(2) Å, *b* = 17.601(2) Å, *c* = 13.6878(13) Å, β = 92.532(4)°, and *Z* = 24. The final reliable index is 0.0406 for 5997 reflections. The molecules are linked through intermolecular N—H…O hydrogen bonds into three-linked molecules forming a supramolecular ring.

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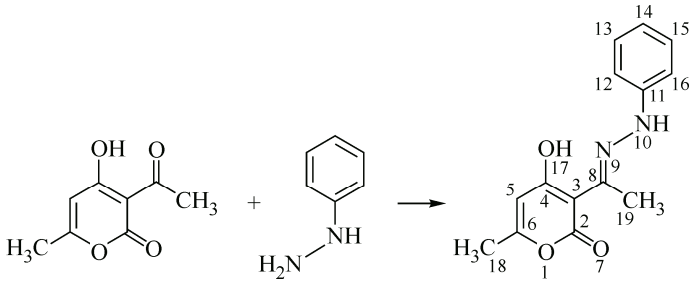
Keywords: single X-ray crystal structure, Schiff base, ESI-mass spectrometry.

Dehydroacetic acid and its derivatives [1—3] form a uniquely important class of compounds due to their wide range of applications. They are potent antifungal and antibacterial [4, 5] agents and their metal complexes have found applications as therapeutic agents against bacteria based on selective DNA cleavage ability [6]. The Schiff base, 4-hydroxy-6-methyl-3-[(1*E*)-1-(2-phenylhydrazinylidene)ethyl]-2*H*-pyran-2-one (DHAA-PH) was prepared as a part of an on-going research on the study of the ligating abilities of this class of compounds towards metal fragments and the antimicrobial properties of the compounds and the metal complexes. The nature of hydrogen bonding is one of the major factors that govern the overall structure and functionality of biologically important molecules [7].We are interested in understanding the nature of the hydrogen bonding within and between the molecules of the compound. We report herein the crystal structure of hydrazone derived from dehydraoacetic acid and phenyl hydrazine.

Experimental. The title compound was synthesized by a modification of the literature procedure [8] in accordance with Scheme 1. Melting point was determined with a Gallenkamp melting point apparatus. The starting materials (dehydroacetic acid and phenylhydrazine) were purchased from Sigma-Aldrich. Methanol and $CDCl_3$ were used as supplied by Celdon Laboratories and Sigma-Aldrich respectively. The IR spectrum was obtained as a KBr disc with a Perkin Elmer Spectrum FTIR spectrometer, version 10.4.3 with a range 4000—400 cm^{-1}. The NMR spectra were recorded on a Bruker Avance 300 MHz spectrometer. Electrospray ionization mass spectra (ESI-MS) were collected on a Waters Micromass Q-ToF spectrometer in positive ion mode using a syringe pump: capil-



Scheme 1. Synthesis and carbon atom numbering of
4-hydroxy-6-methyl-3-[(1*E*)-1-(2-phenylhydrazinylidene)ethyl]-2*H*-pyran-2-one

lary voltage 2900 V; sample cone voltage 15 V; extraction voltage 0.5 V; source temperature 92 °C; desolvation temperature 192 °C; cone gas flow 100 L/h; desolvation gas flow 200 L/h; collision voltage 2 V; MCP voltage 2400 V. The masses were identified by comparing the high resolution mass spectral (HR-MS) isotope patterns with computer modelled isotope patterns [9].

Synthesis of 4-hydroxy-6-methyl-3-[(1*E*)-1-(2-phenylhydrazinylidene)ethyl]-2*H*-pyran-2-one. A solution of phenylhydrazine (168 mg, 1 mmol) was added to a clear stirring solution of dehydroacetic acid (172 mg, 1 mmol) in methanol (25 mL). The mixture was refluxed for 3 h, and the resulting solution was left to cool to room temperature overnight to obtain yellow crystals of the product. The product was filtered, dried, and recrystallized from methanol to give 80 % yield, 206.6 mg. Melting point: 188—190 °C. ^{1}H NMR ($CDCl_3$): δ 2.18 (s, 3H, H_3C-19), 2.74 (s, 3H,H_3C-18), 5.81 (s, 1H, HC-5), 6.50 (s, 1H, HN), 6.88—7.33 (m, 6H, Ar, NH). ^{13}C NMR ($CDCl_3$): δ 15.90 (H_3C-19), 19.87 (H_3C-18), 96.26 (C-3), 105.27 (C-5), 113.40 (C-12, C-16), 122.07 (C-14), 129.64 (C-13, C-15), 144.60 (C-11), 163.12 (C-2), 168.65 (C-6), 180.40 (C-4). FT-IR (KBr, cm^{-1}): 1601 ν(CH—N), 1, 684 ν(C=O), 3055 ν(C–H), 3300 ν(NH), 3455 ν(OH). ESI-MS: *m*/*z* = 259.08, 100 % [M + H].

X-ray structure determination. Crystals suitable for the X-ray crystallographic structure determination were obtained by slow evaporation of a methanol solution at room temperature for 48 h. An arbitrary sphere of data were collected on a colourless block-like crystal, having approximate dimensions of 0.131×0.129×0.092 mm, on a Bruker Kappa X8 APEX-II diffractometer, with λ(MoK_α) = = 0.71073 Å, using a combination of ω- and φ-scans of 0.5° [10]. Data were corrected for absorption and polarization effects and analyzed for the space group determination. The structure was solved by intrinsic phasing methods and expanded routinely [11]. The model was refined by the full-matrix least-squares analysis of F^2 against all reflections using the SHELX suite of programs [11]. All non-hydrogen atoms were refined with anisotropic thermal displacement parameters. Unless otherwise noted, hydrogen atoms were included in calculated positions. Thermal parameters for the hydrogen atoms were tied to the isotropic thermal parameter of the atom to which they are bonded (1.5× for methyl, 1.2× for all others). Hydrogen atoms were located from a difference Fourier map on O3/O3A/O3B oxygen atoms and N2/N2A/N2B hydrazine nitrogen atoms. The hydroxyl hydrogen atoms were subsequently refined as a riding model while the amide hydrogen atoms were allowed to freely refine. The crystal data and structure refinement parameter details: $C_{14}H_{14}N_2O_3$, M = 258.27, 120(2) K, monoclinic, space group $C2/c$, a = 30.011(2) Å, b = 17.601(2) Å, c = 13.6878(13) Å, β = = 92.532(4)°, V = 7223.3(13) Å^3, Z = 24, d_c = 1.425 g/cm^3, μ = 0.102 mm^{-1}, F(000) = 3264, θ ≤ 27.25°, index ranges $-38 \le h \le 38$, $-12 \le k \le 22$, $-17 \le l \le 17$, 52932 reflections collected, 8053 independent (R_{int} = 0.0420), 0 restraints, 538 parameters, GOOF = 1.019, R_1 = 0.0406, wR_2 = 0.1000 (5997 $I > 2\sigma(I)$), R_1 = 0.0618, wR_2 = 0.1114 (all data), $\Delta\rho_{max}$ = 0.288, $\Delta\rho_{min}$ = –0.213 e/Å^3.

Crystal structure of DHAA-PH. There are three crystallographically independent molecules. Bond distances within the pyran ring system reflect a delocalized nature of the bonds, rather than the discrete double/single bond character. The phenylhydrazine moiety is expectedly not planar but adopts a *trans*-conformation about the N1—N2 bond, presumably due to the steric repulsion resulting from the interaction between the methyl and phenyl groups. This *trans*-conformation is also observed in

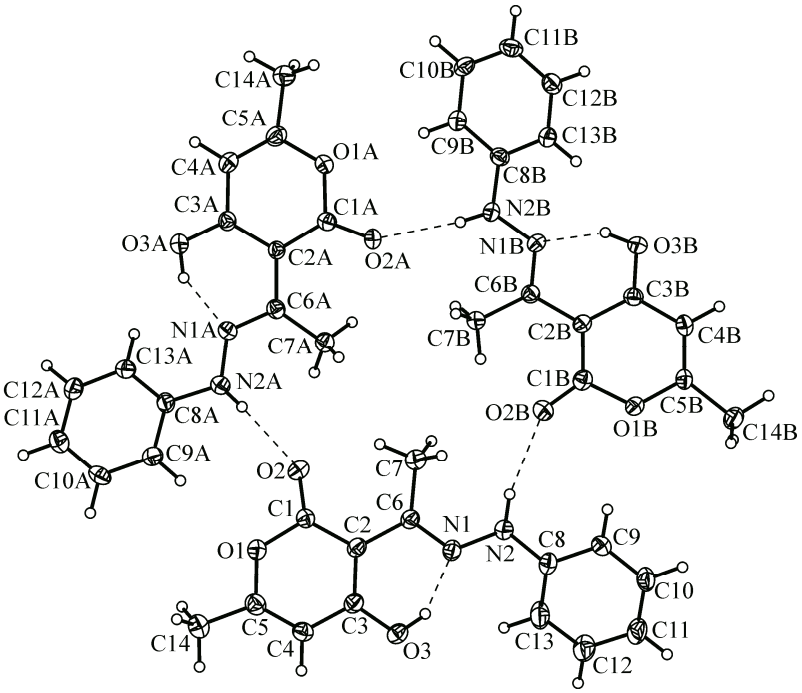


Fig. 1. Molecular structure of the compound with thermal ellipsoid at 50 % probability level with inter- (N—H…O) and intra- (O—H…N) molecular hydrogen bonds shown in dashed lines

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Intra-intermolecular hydrogen bond distances and bond angles

D—H…A	*d*(D—H)	*d*(H…A)	*d*(D…A)	∠(DHA)
O(3)—H(3O)…N(1)	0.84	1.72	2.4702(16)	146.9
O(3A)—H(3OA)…N(1A)	0.84	1.69	2.4385(16)	147.7
O(3B)—H(3OB)…N(1B)	0.84	1.71	2.4642(16)	147.4
N(2)—H(2N)…O(2B)	0.885(19)	2.227(19)	3.0966(17)	167.4(16)
N(2A)—H(2NA)…O(2)	0.87(2)	2.12(2)	2.9720(17)	164.6(17)
N(2B)—H(2NB)…O(2A)	0.874(19)	2.203(19)	3.0252(17)	156.7(17)
C(7)—H(7B)…O(2)	0.98	2.09	2.861(2)	134.7
C(9)—H(9A)…O(1B)	0.95	2.58	3.5035(19)	164.0
C(7A)—H(7AC)…O(2A)	0.98	2.25	2.8721(19)	120.5
C(9A)—H(9AA)…O(1)	0.95	2.49	3.4170(19)	164.7
C(7B)—H(7BC)…O(2B)	0.98	2.20	2.8715(18)	124.4
C(9B)—H(9BA)…O(1A)	0.95	2.56	3.4753(19)	161.3

analogous benzopyrane-2-one derivatives [13—16]. Both N1 and N2 sites act as hydrogen bond partners, with hydroxyl O3 forming an intramolecular hydrogen bond to hydrazine nitrogen N1 (Table 1). Hydrazine nitrogen N2 forms an intermolecular hydrogen bond to pyran carbonyl oxygen O2 on an adjacent molecule. The overall motif is a hydrogen-bonded trimer, supramolecular ring (Fig. 1). These H-bonded molecules are all in general positions and are not related by symmetry.

Supplementary materials. Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication No. CCDC1413252. Copies of this data can be obtained free of charge *via* www.ccdc.cam.ac.uk/data_request/cif, by

emailing data_request@ ccdc.cam.ac.uk, or by contacting the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44 1223 336033.

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