

limits of experimental error. The observed propenide N(7)—C(8) and N(7)—C(13) bond lengths of 1.30 (2) and 1.32 (2) Å indicate partial double-bond character. All cyanide C≡N bonds range from 1.11 (2) to 1.16 (2) Å and are typical triple bonds. The distances C(8)—C(11) and C(13)—C(14) at 1.48 (2) and 1.47 (2) Å are only a little shorter than for a pure single bond, but C(8)—C(9) and C(13)—C(16) at 1.38 (2) and 1.39 (1) Å are significantly shorter. There is a high degree of π -electron delocalization in the tetracyanoazapropenide anion which may be satisfactorily expressed by (VIII).

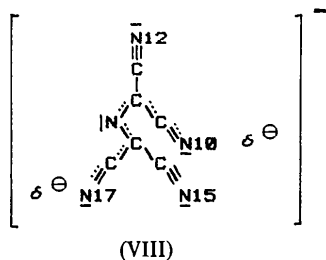


Table 2 shows possible hydrogen bonds and close interionic C—H \cdots N contacts. The shortest H \cdots N

distances involve N(17) and N(19) which do not take part in the conjugation.

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Structure of the *N,N'*-Dimethyl Diimine of 3-[3-(2-Hydroxyphenyl)-3-oxo-1-phenylpropyl]flavanone, the Adduct of Flavanone and 2'-Hydroxychalcone

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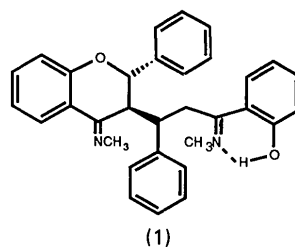
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Abstract. 2-[3-(2,3-Dihydro-4-methylimino-2-phenyl-4*H*-1-benzopyran-3-yl)-1-methylimino-3-phenylpropyl]phenol, $C_{32}H_{29}N_2O_2$, (1), $M_r = 473.60$, monoclinic, $P2_1/c$, $a = 10.090$ (4), $b = 16.662$ (9), $c = 16.478$ (9) Å, $\beta = 114.68$ (3)°, $V = 2517$ (2) Å³, $Z = 4$, $D_x = 1.251$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.7107$ Å, $\mu = 0.43$ cm⁻¹, $F(000) = 1004$, $T = 123$ K, $R = 0.0423$ for 3482 unique observed reflections with $I > 3\sigma(I)$. The structure consists of a flavanone unit linked by its α -carbon [C(3)] to the β -carbon [C(3)] of a 2'-hydroxydihydrochalcone unit, with both carbonyl groups present as their methylimino derivatives. The hydroxy hydrogen is intramolecularly hydrogen bonded to the adjacent imino nitrogen.

Introduction. During the course of imine preparations involving reaction of 2'-hydroxychalcone with

amines, we found in the methylamine case that leaving the reaction solution for a long period resulted in the formation of a byproduct in which two chalcone units are linked, one as a flavanone to the other as a dihydrochalcone. Although such structures are not known to us in natural product chemistry, the potential simplicity of their formation through the conjugate addition of a flavanone to a chalcone makes the current structure of more than novel interest.



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Experimental. The title compound (1) was prepared by adding a tenfold molar excess of methylamine (33% in ethanol) to a saturated solution of 2'-hydroxychalcone in ethanol. After standing for 30 days, the reaction vessel was opened to air. After another 30 days, ethyl acetate was added to the residue, and yellow crystals, m.p. 439–442 K, separated in *ca* 10% yield. The ^{13}C NMR spectrum* showed 32 carbon signals (two chalcone units). X-ray-quality yellow crystals were obtained from toluene–hexane (vapour diffusion). Nicolet XRD P3 four-circle diffractometer, graphite-monochromated Mo $K\alpha$, lattice parameters from least-squares refinement of 25 high-angle reflections, ω scan technique (4996 reflections, 4411 unique $R_{\text{int}} = 0.016$), $5 < 2\theta < 50^\circ$, h 0→13, k 0→20, l -20→20. Space group uniquely determined as $P2_1/c$ from systematic absences. Data corrected for Lp effects but not for absorption. Structure solved by direct methods and refined by full-matrix least-squares procedures based on F (Sheldrick, 1976) with all non-H atoms assigned anisotropic temperature factors. H atoms were included in calculated positions with common fixed temperature factors for each type, except the hydroxy H atom which was located in a penultimate difference map and was refined with a fixed temperature factor; 153 parameters refined. Final $R = 0.0423$ for 3482 reflections with $I > 3\sigma(I)$, $wR = 0.0480$, $w = [\sigma^2(F) + 0.001(F)^2]^{-1}$. The largest Δ/σ in the final cycle (0.2) involved a rotational coordinate of a methyl group, and the largest peak in a final difference map was $0.27 \text{ e } \text{\AA}^{-3}$. Scattering factors were from *International Tables for X-ray Crystallography* (1974, Vol. IV). Atomic coordinates are listed in Table 1,† selected bond lengths and angles in Table 2, and the atom-labelling scheme is shown in Fig. 1.

Discussion. The molecule is envisaged as being formed by conjugate addition to the enone function of one chalcone molecule (or its imine) by the enolate (or enamine) of a flavanone molecule pre-formed by cyclization under the basic conditions (Old & Main, 1982) of a second chalcone molecule. The location of

* ^{13}C NMR (CDCl_3 , 90 MHz) δ 172.9 (*s*, C30), 164.9 (*s*, C18), 160.9 (*s*, C27), 155.4 (*s*, C6), 139.7, 138.9 (both *s*, C7,19), 132.8 (*d*, C4), 132.1 (*d*, C16), 129.3 [*d*, C21(23)], 128.6 [*d*, C8(12)], 128.6 (*d*, C10), 128.3 (*d*, C2), 128.0 (*d*, C14), 127.6 [*d*, C9(11)], 126.0 (*d*, C22), 125.0 [*d*, C20(24)], 121.8 (*s*, C1), 121.5 (*d*, C5), 119.1 (*d*, C3), 117.3 (*s*, C13), 117.3 (*d*, C17), 116.5 (*d*, C15), 77.3 (*d*, C25), 44.8 and 43.7 (both *d*, C26,28), 38.8 (*q*, C32), 34.9 (*q*, C31), 31.4 (*t*, C29).

† Lists of thermal parameters, hydrogen-atom positions, full bond lengths and angles, and structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53137 (24 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Final positional and equivalent isotropic thermal parameters* (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}^*
O(1)	0.4807 (1)	0.16371 (7)	0.77073 (7)	0.027
O(2)	0.0036 (1)	0.14432 (7)	0.31777 (7)	0.030
H(1)	-0.053 (3)	0.174 (2)	0.352 (2)	0.079
N(1)	0.1188 (2)	0.08157 (8)	0.80273 (9)	0.027
N(2)	-0.0805 (2)	0.19363 (9)	0.42972 (9)	0.028
C(1)	0.3224 (2)	0.0527 (1)	0.7701 (1)	0.024
C(2)	0.3006 (2)	-0.0302 (1)	0.7626 (1)	0.029
C(3)	0.3991 (2)	-0.0810 (1)	0.7506 (1)	0.034
C(4)	0.5233 (2)	-0.0488 (1)	0.7462 (1)	0.036
C(5)	0.5477 (2)	0.0324 (1)	0.7528 (1)	0.031
C(6)	0.4479 (2)	0.0833 (1)	0.7647 (1)	0.025
C(7)	0.4488 (2)	0.2278 (1)	0.8949 (1)	0.026
C(8)	0.5322 (2)	0.1699 (1)	0.9556 (1)	0.032
C(9)	0.5906 (2)	0.1858 (1)	1.0467 (1)	0.039
C(10)	0.5665 (2)	0.2588 (1)	1.0782 (1)	0.040
C(11)	0.4817 (2)	0.3160 (1)	1.0185 (1)	0.037
C(12)	0.4231 (2)	0.3003 (1)	0.9272 (1)	0.030
C(13)	0.0956 (2)	0.0914 (1)	0.4674 (1)	0.024
C(14)	0.1868 (2)	0.0340 (1)	0.5273 (1)	0.027
C(15)	0.2676 (2)	-0.0199 (1)	0.5035 (1)	0.031
C(16)	0.2577 (2)	-0.0187 (1)	0.4164 (1)	0.034
C(17)	0.1679 (2)	0.0359 (1)	0.3553 (1)	0.031
C(18)	0.0869 (2)	0.0915 (1)	0.3789 (1)	0.024
C(19)	0.1647 (2)	0.2884 (1)	0.6176 (1)	0.022
C(20)	0.2341 (2)	0.3159 (1)	0.5652 (1)	0.029
C(21)	0.2252 (2)	0.3960 (1)	0.5399 (1)	0.034
C(22)	0.1463 (2)	0.4496 (1)	0.5660 (1)	0.033
C(23)	0.0733 (2)	0.4229 (1)	0.6159 (1)	0.032
C(24)	0.0828 (2)	0.3434 (1)	0.6417 (1)	0.027
C(25)	0.3902 (2)	0.2174 (1)	0.7943 (1)	0.023
C(26)	0.2283 (2)	0.1932 (1)	0.7483 (1)	0.022
C(27)	0.2134 (2)	0.1085 (1)	0.7769 (1)	0.023
C(28)	0.1767 (2)	0.2009 (1)	0.6450 (1)	0.022
C(29)	0.0325 (2)	0.1552 (1)	0.5901 (1)	0.024
C(30)	0.0088 (2)	0.1489 (1)	0.4931 (1)	0.024
C(31)	0.0061 (2)	0.1353 (1)	0.8054 (1)	0.034
C(32)	-0.1767 (2)	0.2523 (1)	0.4425 (1)	0.039

* U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table 2. *Selected bond lengths* (\AA) *and angles* ($^\circ$)

C(1)—C(27)	1.479 (2)	C(13)—C(18)	1.425 (2)
O(1)—C(6)	1.374 (2)	C(13)—C(30)	1.474 (2)
O(1)—C(25)	1.442 (2)	C(25)—C(26)	1.540 (2)
O(2)—C(18)	1.337 (2)	C(26)—C(27)	1.514 (2)
N(1)—C(27)	1.278 (2)	C(26)—C(28)	1.563 (2)
N(1)—C(31)	1.462 (2)	C(28)—C(29)	1.554 (2)
N(2)—C(30)	1.293 (2)	C(29)—C(30)	1.517 (2)
N(2)—C(32)	1.454 (2)	H(1)⋯N(2)	1.46 (3)
H(1)—O(2)	1.08 (3)		
C(6)—O(1)—C(25)	117.6 (1)	N(1)—C(27)—C(26)	128.0 (1)
C(27)—N(1)—C(31)	119.6 (1)	C(1)—C(27)—C(26)	112.8 (1)
C(30)—N(2)—C(32)	123.5 (1)	C(19)—C(28)—C(26)	110.6 (1)
O(1)—C(25)—C(7)	111.3 (1)	C(19)—C(28)—C(29)	111.0 (1)
O(1)—C(25)—C(26)	111.5 (1)	C(26)—C(28)—C(29)	113.5 (1)
C(7)—C(25)—C(26)	114.6 (1)	C(28)—C(29)—C(30)	110.1 (1)
C(25)—C(26)—C(27)	108.3 (1)	N(2)—C(30)—C(13)	116.1 (1)
C(25)—C(26)—C(28)	108.5 (1)	N(2)—C(30)—C(29)	124.1 (1)
C(27)—C(26)—C(28)	112.6 (1)	C(13)—C(30)—C(29)	119.7 (1)
N(1)—C(27)—C(1)	119.1 (1)	N(2)—H(1)—O(2)	154 (2)

the intramolecularly hydrogen-bonded H atom, H(1), allows comparison of the corresponding bond angle [N(2)—H(1)⋯O(2), 154 (2°)] with that for similar intramolecular hydrogen bonding of OH and C=O functions in other flavonoid systems. In 2',6'-dihydroxy-2,4,6-trimethoxychalcone (Miles, Main & Nicholson, 1989a) the CO⋯H—O bond angle is 161° but there will be some influence of concomitant intermolecular hydrogen bonding of

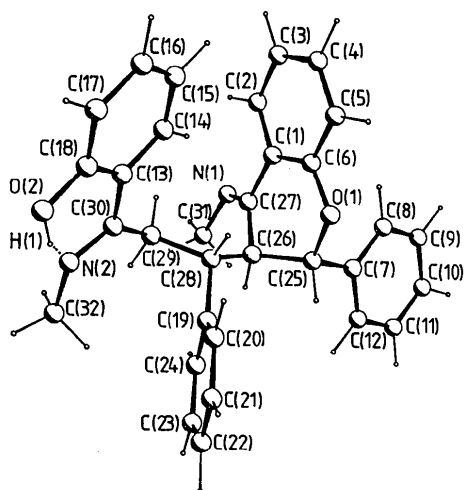


Fig. 1. A PLUTO diagram of the structure showing the atom-labelling scheme.

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Structure of 5-Hydroxyindole-3-acetic Acid

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Abstract. C₁₀H₉NO₃, *M_r* = 191.19, monoclinic, *P*2₁/*c*, *a* = 5.892 (1), *b* = 5.141 (1), *c* = 29.305 (6) Å, β = 102.61 (3)°, *V* = 866.3 (3) Å³, *Z* = 4, *D_m* = 1.439 (2), *D_x* = 1.466 g cm⁻³, λ(Cu *K*α) = 1.5418 Å, μ = 8.74 cm⁻¹, *F*(000) = 400, *T* = 293 K, final *R* = 0.053 for 1420 (*|F_o* > 0.0) independent reflections. The molecule takes a planar conformation, in which the dihedral angle between the indole ring and the carboxyl group is 175.5 (3)°. The molecules in the crystal are held by hydrogen bonds between the centrosymmetrically related carboxyl groups (forming 'cyclic dimers'), between the hydroxyl groups, and between NH(indole) and O(carboxyl).

Introduction. Indole derivatives, widely distributed in living cells as tryptophan metabolites, have important biological functions.

5-Hydroxyindole-3-acetic acid (5-HIAA) is excreted into urine as a major metabolite of serotonin. Since the biological activity (plant growth hormone) of indole-3-acetic acid (IAA), a related

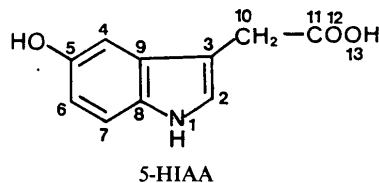
the OH oxygen to another OH group. For 5-hydroxy-7,4'-dimethoxyflavanone (Miles, Main & Nicholson, 1989*b*) the CO...H—O angle is 148°.

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final metabolite of tryptophan, is closely related to the molecular conformation (Kaethner, 1977; Farrimond, Elliott & Clack, 1978), it is important to investigate the molecular conformation of 5-HIAA in considering its biological functions.



Experimental. Crystals were grown as needles from an ethanol/butanol (1:1) mixture by slow evaporation at 293 K. Crystal density was measured by the flotation method using a C₆H₆–CCl₄ mixture. A single crystal with approximate dimensions 0.2 × 0.1 × 0.4 mm was mounted on a Rigaku AFC-5 diffractometer with graphite-monochromated Cu *K*α radiation. Cell parameters were refined by the