Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: BM1032). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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A Trimer from 5,5-Dimethylcyclohexan-1,3-dione Containing an O-Protonated Furan Ring

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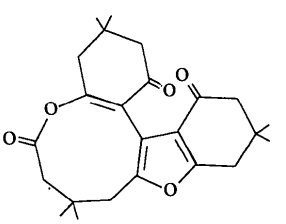
Abstract

Reaction of 5,5-dimethylcyclohexan-1,3-dione with ammonia in ethanol gave a trimer, 1,2,3,4,6,7,8,9,11,12,-13,14-dodecahydro-3,3,8,8,12,12-hexamethyl-1,6,14-trioxobenzo[*b*]benzo[4,5]furo[3,2-*d*]oxoninium hydroxide, $C_{24}H_{31}O_5^+.0.41OH^-$, containing a nine-membered lactone ring and a furan as well as two cyclohexane groups. The furan ring is partially protonated at the O atom with a disordered hydroxide counterion.

Comment

β-Diketones are among the classic ligands of inorganic chemistry but there have been few attempts to prepare complexes of metal ions with cyclic β-diketones such as cyclohexane-1,3-dione (CHD), where the bridgehead methine C2 must present severe steric problems for chelation and bridging between metals is more likely. Colour changes in solution and some early equilibrium studies (Luehrs, Iwamoto & Kleinberg, 1965) indicate that complexes do form but as yet only very poor quality crystals have been obtained in our laboratory. Structures of CHD and of several substituted forms have been reported. These show that the enol form, which predominates in solution, is also found in the solid state (Singh & Calvo, 1975; Etter, Urbanczyk-Lipkowska, Jahn & Frye, 1986; Katrusiak, 1990; Barnes, 1995). The title compound, (I), was the unexpected result of an attempt to crystallize an ammonium salt of dimedone, 5,5-dimethyl-CHD. Ring opening and ring fusion have produced a trimer containing a nine-membered lactone ring and a furan as well as two cyclohexane groups.



(I)

Excluding the peripheral methyl groups, all but three of the non-H atoms can be fitted by only three planes, *A* (O6, C7, C8, O26), *B* (C10, C11, O12, C13, C14, C16, C17, C18, C19, C20, O29) and *C* (C1, C2, C4, C5, O6, C19, C20, O21) with r.m.s. deviations 0.035, 0.054 and 0.060 Å, respectively. The maximum deviation is 0.108 Å for C20. The angle between *A* and *B* is 19.29 (8)°, and between *B* and *C* is 86.35 (4)°. The nine-membered lactone can be described as an eight-membered tub plus C9 forming a prow to place the methyl groups C24 and C25 *exo* to the ring. The angle between the base of the tub (O6, C7, C11, C19) and the prow (C8, C9, C10) is 5.5 (1)°.

No pK_a value is available for the very weakly basic O atom in the furan. Protonation usually occurs not at an O atom but at an α-C atom (Joule, Mills & Smith, 1995). NMR data show protonation at carbon to give a stable cation from 2,5-di-*tert*-butylfuran in solution (Carmody *et al.*, 1976). In (I), there is clear evidence for

O-protonation of the furan ring. Difference maps show a peak at 1.12 (1) Å along the bisector of the C11—O12—C13 angle which refines as an H atom with a small atomic displacement parameter. O29 of the molecule at x, $1.5 - y$, $z - 0.5$ is 1.71 (1) Å from this atom, with O12—H12···O29′ 176.3 (4)°.

O30 shows only one proton in a difference map, as expected for an OH^- counterion. O30 is disordered over two sites 2.080 (11) Å apart and related by a centre of inversion. Each O30 site has the O21 atom of one molecule at 2.632 (6) Å and O21′ (related by the centre of inversion) at 2.678 (6) Å. The position of H30, with O30 at 1.195 (12) Å, O30′ at 1.352 (12) Å and O21 at 1.712 Å, suggests a bifurcated hydrogen bond. The site occupancy of O30 refined to 40.6 (9)%, thus up to 60% of the furan molecules cannot be protonated.

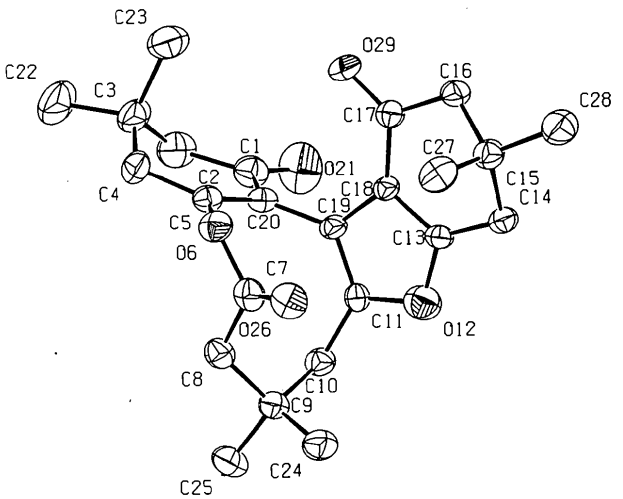


Fig. 1. The title cation with ellipsoids plotted at the 50% probability level.

Experimental

Sample prepared by adding 0.5 ml 0.880 ammonia to 5.0 mmol dimedone in ethanol. The thin plates which grew over some days were recrystallized by allowing water vapour to diffuse into an ethanol solution. Samples for diffractometry were mounted in oil drops before cooling to 150 K.

Crystal data

$C_{24}H_{31}O_5^+.0.41OH^-$
$M_r = 406.79$
Monoclinic
$P2_1/c$
$a = 6.9030\ (10)$ Å
$b = 22.275\ (2)$ Å
$c = 14.6622\ (9)$ Å
$\beta = 95.722\ (11)°$
$V = 2243.3\ (4)$ Å^3
$Z = 4$
$D_x = 1.204$ Mg m^{-3}
Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 250 reflections
$\theta = 2$–$25°$
$\mu = 0.084$ mm^{-1}
$T = 150\ (1)$ K
Plate
0.30 × 0.26 × 0.09 mm
Pale yellow

Data collection

Enraf–Nonius CAD-4 FAST area-detector diffractometer
Area-detector scans
Absorption correction: none
7873 measured reflections
3481 independent reflections
2306 observed reflections $[I > 2\sigma(I)]$
$R_{int} = 0.0664$
$\theta_{max} = 24.90°$
$h = -7 \rightarrow 7$
$k = 0 \rightarrow 26$
$l = 0 \rightarrow 16$
Intensity decay: insignificant

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.056$
$wR(F^2) = 0.157$
$S = 0.85$
3467 reflections
280 parameters
H atoms positioned using a riding model, H12 and H30 refined
$w = 1/[\sigma^2(F_o^2) + (0.0921P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = -0.04$
$\Delta\rho_{max} = 0.26$ e Å^{-3}
$\Delta\rho_{min} = -0.33$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$

	x	y	z	U_{eq}
C1	0.4211 (4)	0.58598 (12)	0.0610 (2)	0.0412 (6)
C2	0.5342 (4)	0.54136 (12)	0.1221 (2)	0.0524 (8)
C3	0.6767 (4)	0.57009 (12)	0.1969 (2)	0.0489 (7)
C4	0.8096 (4)	0.61332 (13)	0.1515 (2)	0.0454 (7)
C5	0.7023 (3)	0.65131 (11)	0.07922 (14)	0.0316 (6)
O6	0.8040 (2)	0.70186 (8)	0.05820 (10)	0.0377 (4)
C7	0.8082 (3)	0.71779 (12)	−0.0346 (2)	0.0348 (6)
C8	0.8655 (3)	0.66761 (11)	−0.0949 (2)	0.0360 (6)
C9	0.7493 (3)	0.66114 (11)	−0.19023 (15)	0.0347 (6)
C10	0.5348 (3)	0.64491 (11)	−0.17846 (15)	0.0316 (6)
C11	0.4335 (3)	0.68651 (10)	−0.11964 (14)	0.0266 (5)
O12	0.3456 (3)	0.73957 (9)	−0.15335 (12)	0.0474 (5)
C13	0.2849 (3)	0.77180 (10)	−0.08259 (14)	0.0270 (5)
C14	0.1904 (3)	0.83198 (10)	−0.08958 (14)	0.0304 (6)
C15	0.2226 (4)	0.86514 (11)	0.00343 (14)	0.0349 (6)
C16	0.1748 (4)	0.82201 (11)	0.08063 (15)	0.0339 (6)
C17	0.2783 (3)	0.76187 (11)	0.08392 (15)	0.0288 (5)
C18	0.3283 (3)	0.73943 (10)	−0.00266 (13)	0.0252 (5)
C19	0.4248 (3)	0.68526 (10)	−0.02620 (13)	0.0265 (5)
C20	0.5221 (3)	0.64098 (10)	0.03850 (14)	0.0291 (5)
O21	0.2532 (3)	0.57621 (9)	0.0291 (2)	0.0697 (6)
C22	0.7989 (6)	0.5211 (2)	0.2489 (2)	0.0826 (12)
C23	0.5623 (5)	0.60451 (14)	0.2647 (2)	0.0616 (9)
C24	0.7636 (4)	0.71815 (13)	−0.2477 (2)	0.0450 (7)
C25	0.8400 (4)	0.60877 (13)	−0.2384 (2)	0.0487 (7)
O26	0.7961 (2)	0.76998 (8)	−0.05281 (12)	0.0440 (5)
C27	0.4338 (4)	0.88634 (12)	0.0211 (2)	0.0465 (7)
C28	0.0861 (5)	0.91929 (12)	0.0020 (2)	0.0514 (8)
O29	0.3102 (2)	0.73411 (8)	0.15709 (10)	0.0368 (4)
O30	0.0705 (9)	0.4745 (3)	0.0526 (4)	0.086 (3)

Table 2. *Selected geometric parameters (Å, °)*

C1—O21	1.226 (3)	C10—C11	1.487 (3)
C1—C20	1.464 (4)	C11—C19	1.378 (3)
C1—C2	1.504 (4)	C11—O12	1.396 (3)
C2—C3	1.538 (4)	O12—C13	1.362 (3)
C3—C4	1.528 (4)	O12—O29^i	2.827 (2)
C3—C22	1.533 (4)	C13—C18	1.383 (3)
C3—C23	1.534 (4)	C13—C14	1.490 (3)
C4—C5	1.494 (3)	C14—C15	1.547 (3)

C5—C20	1.345 (3)	C15—C28	1.529 (4)
C5—O6	1.378 (3)	C15—C27	1.530 (4)
O6—C7	1.410 (3)	C15—C16	1.545 (3)
C7—O26	1.194 (3)	C16—C17	1.517 (3)
C7—C8	1.502 (3)	C17—O29	1.239 (3)
C8—C9	1.547 (3)	C17—C18	1.438 (3)
C9—C25	1.529 (3)	C18—C19	1.437 (3)
C9—C24	1.532 (4)	C19—C20	1.482 (3)
C9—C10	1.551 (3)	O21—O30	2.632 (6)
C20—C5—O6	120.6 (2)	C19—C11—O12	108.0 (2)
C20—C5—C4	126.1 (2)	C19—C11—C10	129.3 (2)
O6—C5—C4	113.2 (2)	O12—C11—C10	122.3 (2)
C5—O6—C7	118.8 (2)	C11—C19—C18	106.8 (2)
O26—C7—O6	116.9 (2)	C11—C19—C20	126.0 (2)
O26—C7—C8	127.6 (2)	C18—C19—C20	126.6 (2)
O6—C7—C8	114.4 (2)	C5—C20—C1	118.9 (2)
C7—C8—C9	117.2 (2)	C5—C20—C19	120.7 (2)
C8—C9—C10	109.6 (2)	C1—C20—C19	120.4 (2)
C11—C10—C9	115.4 (2)		
C5—O6—C7—C8	−50.7 (3)	C10—C11—C19—C20	1.4 (4)
O6—C7—C8—C9	137.9 (2)	C11—C19—C20—C5	90.6 (3)
C7—C8—C9—C10	−64.8 (3)	C19—C20—C5—O6	−3.2 (3)
C8—C9—C10—C11	54.5 (3)	C20—C5—O6—C7	−46.0 (3)
C9—C10—C11—C19	−88.4 (3)		

Symmetry code: (i) $x, \frac{3}{2} - y, z - \frac{1}{2}$.

Data were collected with an area-detector system. Cell dimensions were refined from 250 reflections selected from two regions 90° apart and 5° wide at $\kappa = 0°$.

Intensity standards were not measured by the area detector. Possible variations were checked by comparing the intensities of common or symmetry-related reflections as they occur during data collection. In this case no variation was noted.

Data collection: *FAST-MADNESS* system (Enraf–Nonius, 1990). Cell refinement: *FAST-MADNESS* system. Data reduction: *FAST-MADNESS* system. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *PLATON*93 (Spek, 1993).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: LI1137). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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