Short Communication

The Structure of a 2-Oxoperhydro-1,3,5-triazine, the Cycloaddition Product of Diphenyl-*N*-(*p*-tolyl)ketenimine and Chlorosulfonyl Isocyanate

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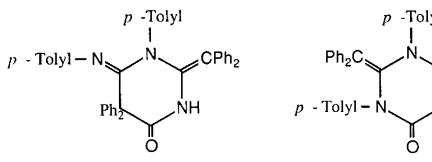
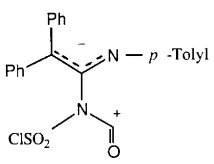
Several years ago we reported on the cycloaddition of isocyanates to ketenimines.[1] Using aromatic isocyanates the product invariably consisted of the corresponding 4-iminoazetidin-2-one derivatives. Alkyl and cyclohexyl isocyanates were unreactive under similar conditions. On the other hand, chlorosulfonyl isocyanate reacted readily with diphenyl-*N*-(*p*-tolyl)ketenimine at 0 °C to give an unstable product from which the chlorosulfonyl group was reductively removed by thiophenol–pyridine.[2] Thus a major stable product was obtained in 84 % yield to which we assigned the structure **1** based on the following evidence. Elemental analysis and mass spectrometry revealed the molecular formula $C_{43}H_{35}N_3O$, corresponding to a combination of two molecules of the ketenimine with one of the isocyanate. In the IR spectrum absorptions due to amide carbonyl, C=C double bonds and amino hydrogens were observed. The ^1H NMR spectrum was in agreement with the structure exhibiting absorptions due to aromatic and methyl protons in the expected ratio, but ^{13}C NMR spectroscopy was not available to us at the time. This spectral information would equally well fit the isomeric structure **2**; however, the mass spectrum gave rise to an ion at *m/z* 194 attributed to ionised diphenylketene, $C_{14}H_{10}O$, which seemed best accommodated by structure **1**. It is reasonable to assume that the zwitterion **3** is initially formed in the reaction between the ketenimine and isocyanate. This intermediate could then react intramolecularly to give the iminoazetidinones or with a second molecule of ketenimine to give either compound **1** or **2**. Thus mechanistically, there was no strong reason to prefer one structure over the other. Since our choice was based entirely on information from the mass spectrum, an investigation by X-ray diffraction was undertaken in order to establish unequivocally the structure of the compound. It showed that the original assignment was indeed wrong and that 4,6-bis(diphenylmethylene)-2-oxo-1,5-ditolylperhydro-1,3,5-triazine (**2**) is actually the major product of the reaction.

Recrystallisation of the compound from acetone resulted in crystals consisting of the compound and the solvent in a 1:1 ratio. The structural investigation revealed that pairs of perhydrotriazine molecules, symmetry-related by two-fold axes, are linked together in the crystal by hydrogen bonds (2.90 Å) between the oxygen atom of one molecule and a nitrogen atom of another and vice versa. They form cavities



1

2



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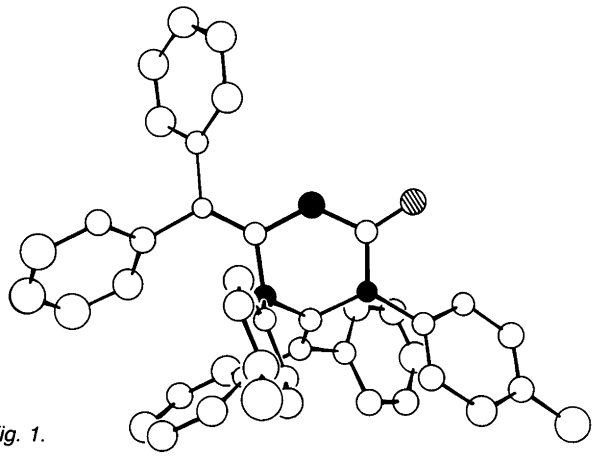

Fig. 1.

within the crystal structure in which acetone molecules of normal geometry are situated with van der Waals' contact. The molecular structure is given in Fig. 1. The molecule is rather crowded, and the central ring conformation seems, at least in part, to be determined by the spatial requirements of the substituents. The four atoms comprising the urea moiety and C-4 from a plane while C-6 and particularly N-5 are positioned out of the plane to allow space for the bulky dipenylmethylene groups (Fig. 2). The phenyl rings of the latter are twisted so as to form an angle of about 90° between the ring planes, which gives rise to precise van der Waals' distances between atoms of neighbouring rings. Furthermore, the C=C double bonds are twisted as well; the torsion angles are measured as 15 and 4.5° for the bonds at C-4 and C-6, respectively.

Experimental

*4,6-Bis(diphenylmethylene)-2-oxo-1,5-di-*p*-tolylperhydro-1,3,5-triazine* (**2**). Diphenyl-*N*-(*p*-tolyl)ketenimine (3.5 g, 12.3 mmol)[3] was dissolved in 50 ml of dry diethyl ether and cooled to −30 °C. Chlorosulfonyl isocyanate (1.74 g, 12.3 mmol) was added with a syringe over 15 min with stirring, during which time a precipitate formed. After the reaction had been stirred for an additional 30 min, the ether was evaporated and replaced by acetone (30 ml). The suspension was cooled in an ice-bath, and thiophenol (2.75 g, 0.025 mmol) was added followed by the dropwise addition of pyridine (1.2 ml) over 15 min. The reaction mixture was left overnight and the precipitated solid was filtered off to yield 3.7 g of a crude product which according to TLC consisted of one major and two minor components. Recrystallisation of this from ethanol gave 3.16 g (84 %) of the major component **2**, m.p. 202–203 °C. The compound crystallised from acetone, m.p. 105–107 °C, by including one solvent molecule (see below). Anal. $C_{43}H_{35}N_3O$: C,H,N. IR: 3210, 1690, 1640, 1610, 1590 cm^{-1}. ^1H NMR (60 MHz, $CDCl_3$): δ 2.12 (s, 3 H), 2.28 (s, 3 H), 6.6–7.4 (m, 29 H). MS [*m/z* (%)]: 209 (68), 207 (21), 298 (13), 283 (100), 257 (11), 194 (4), 165 (70), 64 (48).

X-ray data were collected on a SYNTEX P1 diffractometer using graphite crystal monochromated Mo*K*α radiation (λ = 0.71069 Å).

Large single crystals were obtained by recrystallisation from acetone. The monoclinic crystal used for the diffraction experiments was cut to an irregular shape with the approximate dimensions 0.3×0.4×0.5 mm^3. Conditions for the presence of reflections are $h + k$ even for *hkl* and l even for h 0 l. Intensity statistics gave strong indications of a centric distribution, and the structure determination was carried out assuming the space group to be *C2/c*. The unit cell dimensions were determined to be as follows: a = 20.956(5) Å; b = 13.217(4) Å; c = 29.330(7) Å;

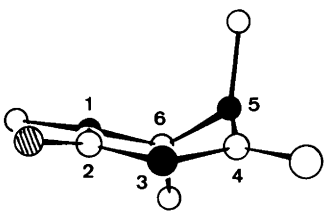

Fig. 2.

Table 1. Fractional coordinates for non-hydrogen atoms. Atoms with one digit indices are atoms of the heterocyclic ring with the two directly attached, non-aromatic carbon atoms and the oxygen atom. The last four entries are acetone atoms.

Atom	*x*	*y*	*z*	*B*
O1	0.49491	0.07521	0.19650	3.5
N1	0.41347	−0.00657	0.21819	2.8
N2	0.32282	−0.07003	0.15745	2.5
N3	0.39185	0.06003	0.14206	2.4
C1	0.35579	−0.06654	0.20788	2.3
C2	0.32399	0.02953	0.13773	2.4
C3	0.43707	0.04482	0.18595	2.6
C4	0.33592	−0.11770	0.23994	2.4
C5	0.27311	0.09221	0.12479	2.7
C11	0.27321	−0.17825	0.22787	2.9
C12	0.27556	−0.28045	0.24013	4.1
C13	0.21646	−0.33842	0.23086	5.3
C14	0.15732	−0.29520	0.21081	5.3
C15	0.15264	−0.19554	0.19763	5.5
C16	0.21106	−0.13635	0.20643	4.0
C21	0.37486	−0.11835	0.29126	2.5
C22	0.34330	−0.09729	0.32540	3.7
C23	0.37755	−0.09949	0.37357	4.4
C24	0.44341	−0.12076	0.38895	4.6
C25	0.47609	−0.14351	0.35625	4.5
C26	0.44151	−0.14427	0.30687	3.7
C31	0.33722	−0.15376	0.13106	2.4
C32	0.32008	−0.15004	0.08169	3.1
C33	0.33322	−0.23134	0.05613	3.8
C34	0.36271	−0.31802	0.07753	3.7
C35	0.37907	−0.32216	0.12688	3.9
C36	0.36730	−0.24137	0.15383	3.3
C37	0.37667	−0.40597	0.04786	6.1
C41	0.28264	0.20197	0.11839	2.7
C42	0.25888	0.24836	0.07377	3.8
C43	0.26652	0.35395	0.06974	4.8
C44	0.29528	0.40794	0.10962	5.1
C45	0.31802	0.36554	0.15286	4.6
C46	0.31168	0.26125	0.15762	3.7
C51	0.20263	0.06079	0.11778	2.7
C52	0.16224	0.12216	0.13473	4.0
C53	0.09639	0.09822	0.12958	4.5
C54	0.06986	0.01063	0.10617	4.9
C55	0.10862	−0.04968	0.08813	4.5
C56	0.17436	−0.02727	0.09378	3.9
C61	0.40796	0.12282	0.10665	2.6
C62	0.38921	0.09084	0.05990	3.5
C63	0.39920	0.15507	0.02451	3.7
C64	0.42721	0.24843	0.03577	3.5
C65	0.44796	0.27594	0.08266	3.9
C66	0.43912	0.21507	0.11838	3.3
C67	0.43544	0.32109	−0.00328	5.6
O2	0.31694	0.06430	0.46734	7.0
C71	0.34848	0.11092	0.44622	5.3
C72	0.31333	0.16522	0.40229	8.0
C73	0.41911	0.11662	0.46517	11.0

$\beta = 107.10(2)°$; $V = 7765(4)$ Å^3. The unit cell contains eight molecules each of the parent compound and of acetone.

Intensity data were collected using the ω-scan technique (scan speed 2° min^{-1}). 3824 reflections with $\sin\theta/\lambda < 0.54$ Å^{-1} were recorded; of these 2463 were larger than 2.5 times their standard deviations and were used for the structure determination. Computer programs used in the calculations are described in the literature.[4,5] The atomic form factors were those of Doyle and Turner,[6] for oxygen, nitrogen and carbon, and of Stewart *et al.*[7] for hydrogen. A starting model for the molecular structure was determined by the use of the program assembly MULTAN[8] and refined by Fourier methods. From the Fourier maps all atoms of the molecular framework were localised and the atomic positions of an acetone molecule were also found. The refinement was carried out using the least-squares method, but as the data were thought to be insufficient for the introduction of anisotropic thermal parameters, only the positional and isotropic thermal parameters of the 51 non-hydrogen atoms were refined. Hydrogen atoms, except for those of the two tolyl methyl groups, were included in calculated positions in the structure factor calculations.

The refinements converged to a conventional R-factor of 0.10 ($R_w = 0.11$). A difference Fourier synthesis revealed some rest electron density (1–2 eÅ^{-3}) which could be interpreted as a disordered acetone molecule in a partly populated position; however, no further refinements were performed. Standard deviations were calculated from the correlation matrix to be in the range 0.009–0.015 Å in interatomic distances and 0.6–1.0° in angles.

The structure factor list may be obtained from the authors upon request. Parameters are given in Table 1.

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