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1,3,5-Tri-*p*-tolylbiuret

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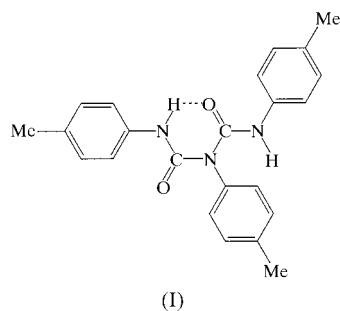
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MoOCl₂(L_{OMe}) as catalyst, where L_{OMe} is CpCo[P(O)(OMe)₂]₃, reacts with *p*-tolyl isocyanate to afford the title compound, C₂₃H₂₃N₃O₂. The structural features are the intramolecular hydrogen bond forming a six-membered ring and a nearly planar arrangement of the biuret moiety. Each *p*-tolyl phenyl ring is twisted by approximately 60–80° with respect to the others. The bond lengths N1–C22 of 1.357 (3) Å and N2–C23 of 1.333 (3) Å indicate that they are partial double bonds.

Comment

4,4'-Methylenebis(phenyl isocyanate) (MDI) is widely known for its use in paints, rigid foams, adhesives, constructions, insulation coatings and related industries (Schollenberger, 1977; Edwards, 1981; Frisch & Reegan, 1973). The current interest in MDI prompted us to investigate the synthesis and reactivity of the isocyanate functional group as well as its physical, mechanical and/or chemical characteristics. The



biuret linkage is important in preparing novel types of polymeric materials as a urea-related connecting block for building the polymer chain. Polybiurets are soluble due to intramolecular hydrogen bonding weakening intermolecular interactions, but polyureas show poor solubility due to strong intermolecular hydrogen bonding (Kurita *et al.*, 1996). The crystal structure of 1,5-diphenylbiuret-*N*-cyano-*N'*-phenylurea has been reported (Yang *et al.*, 1996). 1,3,5-Tri-*p*-tolylbiuret has been characterized previously (Duff & Maciel, 1990), but its crystal structure has not been reported. The title compound, (I), was synthesized from MoOCl₂(L_{OMe}) and *p*-

tolyl isocyanate, and its molecular structure was determined.

The title compound shows an extended conformation and consists of an approximately coplanar fragment including eight atoms (C15, N2, H2N, C23, O2, N3, C22 and O1) with deviations of less than 0.1 Å. The N1–C22 [1.357 (3) Å] and N2–C23 [1.333 (3) Å] bond lengths are in the expected range for partial C–N double bonds (Gilli *et al.*, 1986). The N3–C22 bond length is slightly longer than the N3–C23 bond length due to an intramolecular hydrogen bond [O1...H2N 1.79 (3) Å] which forms a six-membered ring. The C22–N3–C23 [124.6 (2)°] bond angle is comparable with that [126.28 (2)°] of 1,5-diphenylbiuret (Yang *et al.*, 1996) and the N3 atom is almost *sp*² hybridized [N3–C8 1.442 (3), N3–C22 1.401 (3) and N3–C23 1.432 (3) Å; C22–N3–C8 119.4 (2), C23–N3–C8 115.9 (2) and C22–N3–C23 124.6 (2)°]. These facts are expected for the head-to-tail conformation of the two carbonyl groups within the title compound, in contrast to the head-to-head conformation of the two carbonyl groups in 1,5-diphenylbiuret-*N*-cyano-*N'*-phenylurea (Yang *et al.*, 1996). From the crystal structure, the two carbonyl groups in the title compound are not equivalent. However, only a single peak is seen for the carbonyl group in the ¹³C NMR spectrum, which means that there exists a fast dynamic process between two different carbonyl groups. Each *p*-tolyl phenyl ring is twisted by approximately 60–80° with respect to the others.

Experimental

All chemicals were of reagent grade and all solvents were distilled prior to use. MoOCl₂(L_{OMe}) was prepared as described in the literature (Roh & Jeong, 1999). ¹H and ¹³C NMR spectra were recorded on a Varian 300 NMR spectrometer at ambient temperature and chemical shifts were referenced to the internal standard tetramethylsilane. Elemental analyses were performed at the Chemical Analysis Laboratory of the Korea Basic Science Institute at Kyungpook National University. To a solution of MoOCl₂(L_{OMe}) (0.1 g, 0.17 mmol) in 30 ml of dry acetonitrile was added slowly *p*-tolyl isocyanate (1 ml, 7.93 mmol) in 10 ml of dry acetonitrile. The mixture was refluxed for 1 d. After cooling to room temperature, the resulting suspension was filtered off and the solvent was removed *in vacuo* to afford a green solid. The green solid was dissolved in methanol and filtered off. Colourless crystals were obtained from the solution by slow evaporation. An X-ray suitable crystal was obtained by recrystallization from methanol. Yield: 0.435 g (44%). Analysis calculated for C₂₃H₂₃N₃O₂: C 73.97, H 6.20, N 11.25%; found: C 73.98, H 6.23, N 11.21%. ¹H NMR (CDCl₃ at 298 K): δ 8.89 (2H, *br*), 7.32 (8H, *m*), 7.10 (4H, *d*, *J* = 8.1 Hz), 2.44 (3H, *s*), 2.99 (6H, *s*). ¹³C NMR (CDCl₃ at 298 K): δ 153.5, 139.9, 134.7, 134.0, 131.1, 129.5, 120.7, 21.3, 20.8.

Crystal data

C₂₃H₂₃N₃O₂
M_r = 373.44
 Orthorhombic, *P*2₁2₁2₁
a = 9.7626 (6) Å
b = 12.4280 (8) Å
c = 16.6770 (7) Å
V = 2023.4 (2) Å³
Z = 4
D_x = 1.226 Mg m⁻³

Mo *K*α radiation
 Cell parameters from 25 reflections
 θ = 11.16–13.78°
 μ = 0.080 mm⁻¹
T = 293 (2) K
 Tetragonal rod, colourless
 0.50 × 0.45 × 0.45 mm

Data collection

CAD-4 diffractometer
 $\omega/2\theta$ scans
 2308 measured reflections
 2263 independent reflections
 1501 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.006$
 $\theta_{\text{max}} = 25.97^\circ$

$h = -12 \rightarrow 0$
 $k = 0 \rightarrow 15$
 $l = 0 \rightarrow 20$
 2 standard reflections
 frequency: 60 min
 intensity decay: 0.3%

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.033$
 $wR(F^2) = 0.095$
 $S = 0.985$
 2263 reflections
 262 parameters
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0615P)^2P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.12 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.12 \text{ e } \text{\AA}^{-3}$
 Extinction correction: *SHELXL97*
 Extinction coefficient: 0.015 (2)

H atoms on C atoms were constrained using a riding model with $U(\text{H})$ fixed at 1.2 (Ph) or 1.5 (Me) times the U_{eq} of the parent C atoms. H atoms on N atoms were refined isotropically. There were only 35 Friedel pairs in the data set and these were merged. This combination of chemical formula and X-ray wavelength can not give a definitive absolute structure determination; the Flack (1983) parameter refines to a meaningless value of -4 (2).

Data collection: *CAD-4 Software* (Enraf-Nonius, 1989); cell refinement: *CAD-4 Software*; data reduction: *MolEN* (Fair, 1990);

program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997);
 program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997);
 software used to prepare material for publication: *SHELXL97*.

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