Phosphor- oder Stickstoffatome des Kations oder Iodatome benachbarter Anionen. Der kürzeste interionische Abstand beträgt I···H = 3,72 Å. Das Triiodidion bleibt daher unbeeinflußt von elektronischen Wechselwirkungen mit der Umgebung. Es hat den häufig beobachteten asymmetrischen gewinkelten Aufbau, wobei aber die Abstände I—I = 2,896, 2,928 Å und der Bindungswinkel I—I—I = 178,84° nur wenig von denen der gestreckten symmetrischen Anordnung abweichen. Das hier untersuchte Ion ordnet sich folglich in die Reihe der bereits strukturell charakterisierten Triiodide ein (Georgy, 1986). Die geringfügige Verzerrung des Ions läßt sich auf seine irreguläre Umgebung zurückführen. Wie in anderen Strukturen besitzen die terminalen Iodatome größere Temperaturkoeffizienten als das zentrale, was auf thermischen Schwingungen des Anions im Kristall oder auf einer geringfügigen Lagenfehlordnung beruhen kann. Die Struktur des Kations folgt dem bekannten Bild, wie ein Vergleich mit 118 publizierten Strukturen zeigt, für die $R_F \leq 0{,}06$ und P—N—P ≠ 180° ist. Die hier beobachteten Werte N—P = 1,573 Å und P—N—P = 145,2 (3)° stimmen mit den Mittelwerten der angegebenen Daten P—N = 1,58 (2) Å und P—N—P = 143 (6)° hinreichend überein.

Die Vergleichsdaten für das Kation PPN$^+$ entstammen dem Cambridge Data File. Das eingesetzte PPNCl stellte Frau Dr M. von Bruck zur Verfügung. Diese Arbeit wurde durch eine Sachmittelspende des Fonds der Chemischen Industrie gefördert. Wir danken für die Unterstützung.

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Structure of *N*-Methyl-*N*′-phenylurea

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Abstract. $C_8H_{10}N_2O$, $M_r = 150{\cdot}18$, orthorhombic, *Pbca*, $a = 21{\cdot}8632\,(9)$, $b = 9{\cdot}2726\,(5)$, $c = 7{\cdot}7450\,(7)$ Å, $V = 1570{\cdot}1\,(2)$ Å^3, $Z = 8$, $D_x = 1{\cdot}271$ Mg m^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71069$ Å, $\mu = 0{\cdot}08$ mm^{-1}, $F(000) = 640$, room temperature, final $R = 0{\cdot}052$ for 853 observed reflections. The title compound has a *syn–syn* conformation with a planar environment for the N atoms. The interplanar angle between the phenyl group and the urea skeleton is about 30°. The crystal structure is stabilized by the

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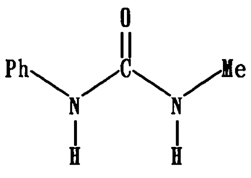
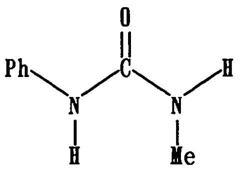
formation of intermolecular N—H···O hydrogen bonds with an H···O distance of 2·12 Å (mean value) and an N—H···O angle of 156° (mean value).

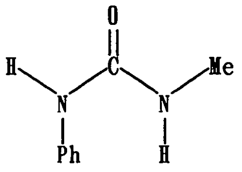
Introduction. Polypeptides and proteins containing an amide group as the main structural element are fixed by N—H···O hydrogen bonds in their framework. Several authors have chosen substituted ureas as relevant models in investigations of these biomolecules (Hallam & Jones 1970; Eaton & Zaw 1976; Mido, Yamanaka & Awata, 1977; Gonzales, Bogdanov, Yutronic & Manzur, 1983). We report here the structure of the unsymmetrically substituted *N*-methyl-*N*′-phenylurea. The conformations of *N*,*N*′-alkylarylureas were studied by IR and ^{1}H NMR techniques (Sudha & Sathyanarayana, 1984) concluding that among the four possible conformations for the title compound (see scheme) in solution, only the *anti–anti* conformation should be destabilized for steric reasons. In order to estimate the favoured conformation in the solid state, we have determined the structure by X-ray diffraction. The title compound was obtained by reductive cleavage of a disubstituted tetrazolium fluorosulfonate. As described (Rochat & Olofson, 1969; Zimmerman & Olofson, 1970), 1,4-disubstituted tetrazolium salts undergo base-induced ring scission to carbodiimides, probably *via* an intermediate ylide. The latter react with water to give urea compounds.



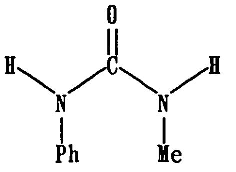
syn–syn



syn–anti



anti–syn



anti–anti

Experimental. *N*-Methyl-*N*′-phenylurea was synthesized by reduction of an isomeric mixture (ratio 1:1) of 1- and 2-methyl-4-phenyltetrazolium fluorosulfonate (Carboni, 1987) with $LiAlH_4$ in ether. After stirring for 16 h, the solution was extracted with water and NaOH (40%). The organic phase was concentrated by evaporation of the solvent, and the crystals grown were washed with dry ether. Crystal size = 0·78 × 0·33 × 0·29 mm, Nicolet *R*3*m*/*V* four-circle diffractometer, ω scan (scan width 1·0°), lattice parameters determined with 35 reflections (20° ≤ 2θ ≤ 25°), no absorption correction applied, maximum value of $(\sin\theta)/\lambda$ = 0·54 Å^{-1}, *hkl* range $0 \le h \le 23$, $0 \le k \le 9$ and $0 \le l \le 8$, two standard reflections (*hkl* = $\bar{3}11$ and $28\bar{2}$) with no significant variation during the experiment, 1228 measured intensities, 1020 unique reflections, 167 unobserved reflections [$F_o \ge 4\sigma(F)$], structure solved by direct methods and full-matrix refinement on *F* with *SHELXTL-PLUS* (Sheldrick, 1988) with rigid group refinement for phenyl C atoms (C—C 1·396 Å, C—C—C 120°). H atoms located from difference Fourier synthesis, refined as rigid groups only for methyl and phenyl groups with unique isotropic temperature factors for methyl, *ortho*, *meta* and *para* phenyl H atoms (C—H 0·96 Å, H—C—H 109·5° for methyl, C—C—H 120° for phenyl), 103 parameters refined, $R = 0{\cdot}052$ and $wR = 0{\cdot}067$ with $w^{-1} = [\sigma^2(F_o) + 0{\cdot}0052F_o^2]$, $(\Delta/\sigma)_{\max} = 0{\cdot}666$, maximum and minimum electron densities based on final difference Fourier synthesis $(\Delta\rho)_{\max} = 0{\cdot}18$ e Å^{-3} and $(\Delta\rho)_{\min} = -0{\cdot}23$ e Å^{-3}, atomic scattering factors from *SHELXTL* (Sheldrick, 1988) and Cromer & Mann (1968), *f*′, *f*″ values from Cromer & Liberman (1970).

Table 1. *Atomic coordinates* (× 10^4) *and equivalent isotropic thermal parameters* (Å^2 × 10^3), *with e.s.d.'s in parentheses*

	x	*y*	*z*	*U**
N(1)	5482 (1)	5081 (3)	2964 (4)	51 (1)
C(2)	5019 (1)	5833 (3)	2291 (3)	43 (1)
N(3)	4519 (1)	5013 (3)	1899 (3)	48 (1)
C(4)†	3946	5499	1295	42 (1)
C(5)†	6061 (1)	5764 (4)	3381 (5)	66 (1)
C(6)	3435 (1)	4679 (2)	1742 (2)	47 (1)
C(7)†	2855	5103	1193	55 (1)
C(8)†	2785	6346	198	58 (1)
C(9)†	3296	7166	−249	54 (1)
C(10)†	3877	6742	300	46 (1)
O(11)	5041 (1)	7149 (2)	2068 (3)	58 (1)
H(1)‡	5428 (14)	4195 (57)	3176 (42)	63 (10)
H(3)‡	4563 (15)	4043 (47)	2051 (47)	78 (11)

* Equivalent isotropic *U* calculated as one third of the trace of the orthogonalized U_{ij} tensor.

† Atoms in rigid groups have standard deviations only for the pivot atom.

‡ Only H atoms involved in N—H···O hydrogen bonds are listed.

Discussion. Final atomic coordinates and equivalent isotropic thermal parameters are listed in Table 1.* Selected bond distances and angles are given in Table

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* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and a complete list of bond lengths and angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52607 (9 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Bond lengths* (Å), *bond angles* (°) *and torsion angles* (°) *for N-methyl-N′-phenylurea* (MePhU), *methyl- and phenylurea, with e.s.d.'s in parentheses*

	MePhU	Methylurea[a]	Phenylurea[b]
N(1)—H(1)	0·846 (43)	0·820 (2)	0·900 (8)
N(1)—C(2)	1·335 (4)	1·336 (2)	1·326 (10)
N(1)—C(5)	1·453 (4)	1·439 (2)	
C(2)—N(3)	1·365 (4)	1·340 (2)	1·375 (10)
C(2)—O(11)	1·234 (3)	1·248 (1)	1·245 (9)
N(3)—H(3)	0·912 (44)	0·850 (2)	0·890 (13)
N(3)—C(4)	1·411 (3)		1·419 (9)
H(1)···O(11*A*)	2·166	2·17 (2)	2·10 (8)
H(3)···O(11*A*)	2·074	2·22 (2)	2·14 (13)
H(1)—N(1)—C(2)	118·5 (22)	115·0 (2)	116·0 (5)
H(1)—N(1)—C(5)	120·2 (21)	122·0 (2)	
N(1)—C(2)—N(3)	113·8 (3)	116·6 (2)	115·0 (7)
N(1)—C(2)—O(11)	122·7 (3)	122·0 (1)	122·5 (7)
C(2)—N(1)—C(5)	121·3 (3)	122·5 (2)	
C(2)—N(3)—H(3)	115·9 (21)	117·0 (2)	114·0 (8)
C(2)—N(3)—C(4)	127·3 (2)		124·4 (6)
N(3)—C(2)—O(11)	123·4 (2)	121·4 (2)	122·6 (7)
H(3)—N(3)—C(4)	116·8 (21)		120·0 (8)
N(3)—C(4)—C(6)	117·0 (1)		116·8 (7)
N(3)—C(4)—C(10)	123·0 (1)		121·0 (6)
N(1)—H(1)···O(11*A*)	154·1	159·0 (2)	154·0 (7)
N(3)—H(3)···O(11*A*)	157·1	151·0 (1)	147·0 (11)
H(1)—N(1)—C(2)—N(3)	−5·0 (3·2)		
H(1)—N(1)—C(2)—O(11)	174·1 (3·2)		
N(1)—C(2)—N(3)—H(3)	−4·7 (3·2)		
N(1)—C(2)—N(3)—C(4)	175·0 (0·3)		
C(2)—N(3)—C(4)—C(6)	−150·0 (0·3)		
N(3)—C(2)—N(1)—C(5)	177·0 (0·3)		
H(3)—N(3)—C(2)—O(11)	176·1 (3·2)		
H(3)—N(3)—C(4)—C(10)	−150·6 (3·2)		
C(4)—N(3)—C(2)—O(11)	−4·2 (0·5)		
C(5)—N(1)—C(2)—O(11)	−3·8 (0·5)		

References: (*a*) Huiszoon & Tiemessen (1976); (*b*) Kashino & Haisa (1977).

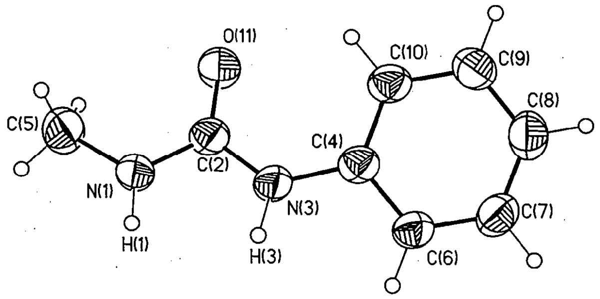

Fig. 1. Perspective view of the molecule showing the atomic labelling. Ellipsoids are drawn to include 50% probability for non-H atoms.

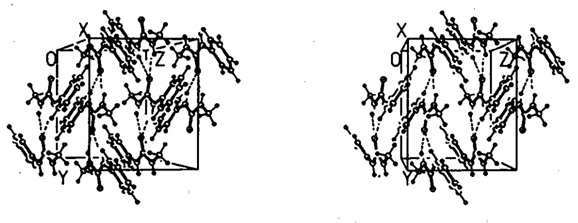

Fig. 2. Stereoview showing the crystal packing along the *x* axis. The broken lines represent hydrogen bonds.

2. The numbering scheme and the geometry of the molecule are shown in Fig. 1. The molecular dimensions of the title compound can be compared with the structures of urea, methylurea and phenylurea. We choose the latter two for comparison.

The bond lengths between the N atoms and the methyl and phenyl groups, respectively, are in the normal range for $N(sp^2)$—$C(sp^3)$ and $N(sp^2)$—$C(sp^2)$ bonds (Rademacher, 1987) which also holds for the C═O bond. The bond lengths between the N atoms and the carbonyl C atom agree well with the observed lengths in methylurea (Huiszoon & Tiemessen, 1976) and phenylurea (Kashino & Haisa, 1977). Thus, the molecular geometry can be regarded as a combination of methyl- and phenylurea. The well known planarity of the urea skeleton in the solid state has been confirmed. There is no distortion from a planar environment at the N atoms and the carbonyl C atom, documented by the sum of bond angles at these atoms (360·0°). As shown in Fig. 1 the molecule has a *syn–syn* conformation with the methyl and the phenyl group orientated towards the O atom. The phenyl group has an interplanar angle of 27·5° to the urea skeleton, reducing the interference of both groups, obviously caused by intramolecular H—H repulsion [H(6)···H(3) 2·39 Å]. The packing is determined by two N—H···O hydrogen bonds arranged along the screw axis parallel to the *y* axis as shown in Fig. 2. The intermolecular H···O distance $(1-x,\ 0{\cdot}5+y,\ 0{\cdot}5-z)$ 2·12 Å (mean value) and the N—H···O angle 156° (mean value) are in accord with hydrogen bridges as observed in other ureas, *i.e.* phenylurea with 2·12 Å and 150·5° (mean values).

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