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Bis(phenyl)-1-carbamoylguanidinium *N*-Phenylcarbamidonitrilate. Revision of an Earlier Proposal

Frank H. Herbstein,[a] Moshe Kapon[a] and Quin-Chuang Yang[b]

[a]*Department of Chemistry, Technion-Israel Institute of Technology, Haifa 32000, Israel, and* [b]*Department of Chemistry, Peking University, Beijing 100871, People's Republic of China. E-mail: chr03fh@tx.technion.ac.il*

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Abstract

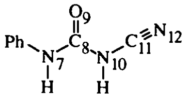
Further refinement of the X-ray diffraction structure factors from the purported neutral molecular complex of 1,5-diphenylbiuret and phenylcarbamidonitrile shows that this material is actually the title salt, $C_{14}H_{15}N_4O^+.C_8H_6N_3O^-$ [IUPAC name: 1-phenyl-3-(*N*-phenylcarbamoyl)guanidinium 3-phenyl-1-ureidonitrilate]. The vital clue was that one of the postulated C—O bond lengths in the presumed 1,5-diphenylbiuret component was too long for a carbonyl group; then unconstrained refinement, without any assumptions, showed that both proton transfer had occurred and the cation was bis(phenyl)-1-carbamoylguanidinium, the postulated C—O group having been replaced by C—NH_2.

Comment

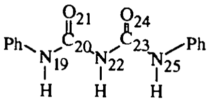
Despite the acceptability of the results of the crystal structure analysis of a proposed molecular complex by almost all the usual criteria, there were some features that suggested to one of us (FHH) that further consideration was necessary. Besides leading to unexpected results regarding the chemical nature of the crystal studied, this work has demonstrated again the power of modern X-ray diffraction methods even when the crucial issue is the location of H atoms in a crystal at room temperature; the *sine qua non* is accurate intensity measurements from a good quality crystal.

The crystal structure of a serendipitously obtained 1:1 hydrogen-bonded molecular complex has been reported recently (Yang, Huang, Chen & Tang, 1996; hereafter YHCT96); the neutral components were inferred to be 1,5-diphenylbiuret [DPB, (II)] and phenycarbamidonitrile [PCN, (I), alternatively named 1-cyano-3-phenylurea]. There are three possible tautomeric forms for each of these components and many conformers. Using the C—O bond length as datum, it was inferred unequivocally' that PCN exists in the carbonyl form both in its neat crystals [d(C—O) = 1.219 (2) Å; Yang, Huang, Chen & Tang, 1995] and in the molecular complex [d(C—O) = 1.233 (3) Å]. YHCT96 considered that DPB occurred as the dicarbonyl tautomer in the molecular complex, with a *syn* conformation ['...the *cis* (*sic*) conformation of the two carbonyls in the molecule of (II)...']. The crystal structures of a number of derivatives of biuret have been reported but not that of DPB itself.

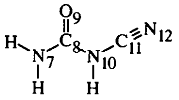
There is, however, a problem with the dicarbonyl proposal for DPB, because only one of the two C—O bond lengths conforms to that expected for a carbonyl group, *i.e.* d(C20—O21) = 1.216 (3) Å, well within the range expected for a carbonyl group, but d(C23—O24) = 1.325 (3) Å, well outside this range but within the range expected for a C—OH group. Thus, the interpretation given by YHCT96 is certainly incorrect and DPB does not exist as the dicarbonyl tautomer in its (so-called) PCN:DPB molecular complex. Our initial hypothesis was that C23—O24 is C—OH and not C═O, with intramolecular C═O···HO—C hydrogen bonding leading to the formation of a six-membered ring analogous to those found in many *cis*-enol systems. However, we could not find an unambiguous interpretation of the available structural results on this basis and hence decided to further refine the structural model.



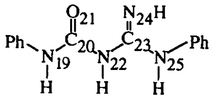
Phenyl carbamidonitrile
Carbonyl tautomer



1,5-Diphenylbiuret
Dicarbonyl tautomer



Cyanourea



Bis(phenyl)-1-carbamoyl guanidine

The X-ray measurements had been made by YHCT96 in Beijing at 296 K with a four-circle diffractometer, using Mo $K\alpha$ radiation; the refinement was carried out on I (intensity) and $R[F > 2\sigma(F)] = 0.0578$. The H-atom parameters were not refined. New measurements were not made but further refinement was carried out in parallel in Beijing and Haifa. The principal (and essential) innovation was that hydrogen parameters were now refined without constraints. The immediate effects were that HN10 vanished from the difference map (density < 0.1 e Å^{-3}) and that two H atoms appeared on either side of the atom labelled as O24, at distances of about 0.9 Å. It was also noticed that the displacement parameter of (so-called) O24 was larger than that of adjacent atoms and it was decided to replace this O atom with an N atom. This resulted in a more reasonable displacement parameter. Each change was carried out separately and checked for a concomitant reduction in R. The parameters of YHCT96 gave (after one cycle of

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refinement) $R(F) = 0.0540$ for the 2971 reflections with $F_o > 4\sigma(F_o)$ and 0.0677 for all 3667 data; $wR(F^2) = 0.1155$ for all data. After the changes described here had been made, the corresponding values were 0.0389, 0.0517 and 0.1007; the final goodness-of-fit (all data) was 1.062 (details of the refinement are given in the *Experimental* section).

We can make a direct comparison between the state of the PCN moiety in the neat crystal (*i.e.* as the neutral molecule) and in the complex (as the anion). Bond lengths and angles are given in Table 1(*a*). The basic difference is the removal of the proton at N10, which causes small but significant geometric changes over the whole molecule except for the phenyl ring. The dihedral angle the phenyl ring makes is 27.6 (4)° in the neutral molecule and 30.5 (4)° in the anion. The parent (*i.e.* unsubstituted) anion is that of cyanourea, the structure of which has been reported in silver cyanourea (Britton, 1987); the agreement is fair [Table 1(*a*)]. Cyanourea is a strong acid and forms many metal complexes.

Component (II), the so-called 1,5-diphenylbiuret moiety, becomes, with replacement of O24 by $N24H_2$, the bis(phenyl) derivative of the 1-carbamoylguanidinium cation. The parent (unsubstituted) moiety has been structurally characterized as the neutral molecule in 1-carbamoylguanidine ethanol solvate (DIVVAF; Begley, Hubberstey & Moore, 1985), as the cation in the perchlorate salt (DIVVEJ; Begley, Hubberstey & Moore, 1985) and as a ligand in a number of copper coordination complexes (Begley, Hubberstey & Moore, 1986; Begley, Hubberstey, Martindale, Moore & Price, 1988). The geometries (*i.e.* bond lengths and angles, and conformations) of the unsubstituted and bis(phenyl) moieties are compared in Table 1(*b*) and show excellent agreement for the two cations.

The calculated chemical analysis percentages for the two formulations (neutral first, followed by ionic) are significantly different for H, N, O: C 63.45, 63.60; H 4.84, 5.09; N 20.18, 23.60; O 11.53, 7.70%. The average of two independent measurements gave C 62.04, H 5.08, N 22.98%. Although the percentage of C is low (and non-discriminatory), the H and N values favour the ionic formulation. The molecular weights of the moieties are significantly different: $C_{14}H_{13}N_3O_2.C_8H_7N_3O$ 255.2278, 161.1641 (total 416.3919); $C_{14}H_{15}N_4O^+.C_8H_6N_3O^-$, 255.3012, 160.1561 (total 415.4573); mass spectromet-

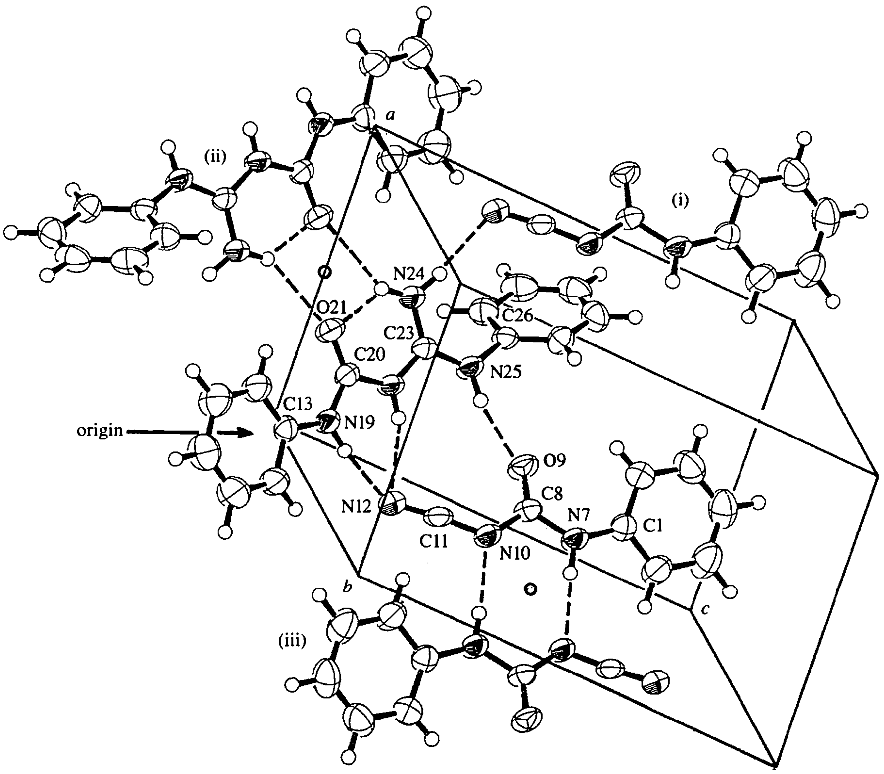

Fig. 1. Partial packing diagram (*ORTEPII*; Johnson, 1976) for bis(phenyl)-1-carbamoylguanidinium phenylcarbamidonitrilate. The numbering of the atoms of the reference moieties and the hydrogen-bonding scheme are shown. The atoms in the phenyl rings have numbers as follows: C1–C6 (anticlockwise), C13–C18 (clockwise) and C26–C31 (anticlockwise). The ellipsoids (differentiated for C, N, O) are drawn at the 50% probability level, H atoms are small spheres of arbitrary radii. Hydrogen bonds are shown as broken lines and symmetry codes (i), (ii) and (iii) are as defined in Table 2. Two centres of symmetry are shown by open circles, while others have been omitted for clarity.

ric measurements were not made. Crystal densities will differ by only 0.25% and were not measured.

There is extensive hydrogen bonding, as noted by YHCT96, and we present an amended scheme (Table 2 and Fig. 1). The reference cation has intramolecular hydrogen bonding between HAN24 and O21 and acts as a donor in intermolecular hydrogen bonding between N19 and N22 to N12 of the reference anion, and between N24 of the reference cation to N12 of another anion; O21 of the reference cation is an acceptor of a hydrogen bond from HAN24 of another cation. Atom N7 of the reference anion acts as a donor to $N10^-$ of another anion, and as an acceptor at O9, $N10^-$ and N12, the latter accepting three hydrogen bonds.

An analogous (hydrogen-bonded) co-crystal of cyanuric acid and biuret is obtained when biuret is recrystallized from methanol–water (2:1 *v*/*v*), whereas biuret crystallized from water gives the monohydrate (Stainton, Harris & Howie, 1991). These authors note that 'the presence of methanol is evidently crucial for the partial decomposition of biuret to cyanuric acid to occur'. This was claimed as the first example of formation of a co-crystal between a molecule and its solution decomposition product; the present system is a further example.

By analogy with 1-carbamoylguanidinium perchlorate, we should place the positive charge on N22 of the bis(phenyl)-1-carbamoylguanidinium cation, but N25 is also a possibility, and perhaps N24 could also be considered. Bond lengths show appreciable delocalization and are not helpful in making a choice. What is the source of the bis(phenyl)-1-carbamoylguanidinium cation? Phenylcarbamidonitrile crystallizes unchanged from tetrahydrofuran but gives CO_2, aniline and cyanamide on boiling with water for a short time (Boeseken, 1897, see p. 353; quoted in Beilstein, **12**, I, 235a); analogous slow decomposition in the presence of water (possibly contained in the solvent) could be anticipated. Presumably the bis(phenyl)-1-carbamoylguanidinium cation results from condensation of phenylcarbamidonitrile and aniline. Incidentally, this cation is not mentioned in either Beilstein or *Chemical Abstracts* so its identification here may be claimed as the first preparation, although hardly as a synthesis.

The material studied by YHCT96 is not a neutral molecular complex but the salt bis(phenyl)-1-carbamoylguanidinium phenylcarbamidonitrilate, with extensive hydrogen bonding between the moieties. This has been demonstrated by unconstrained refinement of the X-ray diffraction data, which are clearly of high quality. The geometric details of cation and anion agree well with those found in analogous moieties.

Experimental

Details of the preparation of the title compound are given in Yang, Huang, Chen & Tang (1996).

Crystal data

$C_{14}H_{15}N_4O^+.C_8H_6N_3O^-$
$M_r = 415.46$
Triclinic
$P\bar{1}$
$a = 7.638\ (2)$ Å
$b = 10.603\ (3)$ Å
$c = 14.364\ (5)$ Å
$\alpha = 107.63\ (2)°$
$\beta = 94.57\ (2)°$
$\gamma = 107.12\ (2)°$
$V = 1041.2\ (5)$ Å^3
$Z = 2$
$D_x = 1.325$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 7.06–10.88°$
$\mu = 0.090$ mm^{-1}
$T = 293\ (2)$ K
Block prism
$0.5 \times 0.5 \times 0.5$ mm
Colourless

Data collection

Siemens *R*3*m*/*V* diffractometer
$\theta/2\theta$ scans
Absorption correction: none
3667 measured reflections
3667 independent reflections
2971 reflections with $I > 2\sigma(I)$

$\theta_{\max} = 25.05°$
$h = 0 \rightarrow 9$
$k = -12 \rightarrow 12$
$l = -17 \rightarrow 16$
2 standard reflections every 100 reflections intensity decay: 1.0%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.039$
$wR(F^2) = 0.101$
$S = 1.062$
3667 reflections
366 parameters
All H atoms refined
$w = 1/[\sigma^2(F_o^2) + (0.0476P)^2 + 0.179P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.045$
$\Delta\rho_{\max} = 0.17$ e Å^{-3}
$\Delta\rho_{\min} = -0.12$ e Å^{-3}
Extinction correction: *SHELXL*93
Extinction coefficient: 0.031 (7)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Comparison of selected bond lengths and angles (Å, °) in various moieties in different crystals, with all the moieties being essentially planar except for the disposition of the phenyl rings (see text and YCHT96)*

(*a*) Selected geometric parameters (Å, °) in analogous portions of phenylcarbamidonitrile (neutral; YCHT96), phenylcarbamidonitrilate (anion; present work) (similar atom numbering is used for both moieties) and the cyanourea anion of silver cyanourea [for numbering, see Scheme, changed from that used by Britton (1987)]. (*b*) Selected geometric parameters (Å, °) in analogous portions of 1-carbamoylguanidine (neutral) in its ethanol complex, bis(phenyl)-1-carbamoylguanidinium (cation) (present work) and 1-carbamoylguanidinium (cation) in its perchlorate salt. For the first and third compounds, the numbering has been changed to match that used in the present paper (see Scheme).

(*a*)

	PCN (neutral)	PCN (anion)	Ag cyanourea
C1—N7	1.425 (3)	1.405 (2)	–
N7—C8	1.339 (3)	1.363 (2)	1.327 (6)
C8—$N10^-$	1.392 (3)	1.373 (2)	1.378 (6)
C8—O9	1.219 (3)	1.232 (2)	1.248 (5)
$N10^-$—C11	1.335 (3)	1.293 (2)	1.295 (6)
C11—N12	1.139 (3)	1.168 (2)	1.149 (6)

C1—N7—C8	126.6 (2)	127.40 (13)	-
N7—C8—N10$^-$	113.4 (2)	111.28 (13)	116.0 (4)
C8—N10$^-$—N7	120.7 (2)	115.15 (13)	115.1 (4)

(*b*)

	1-Carbamoyl-guanidine (neutral)	Bis(phenyl)-1-carbamoyl-guanidinium (cation)	1-Carbamoyl-guanidinium (cation)
C13—N19	-	1.409 (2)	-
N19—C20	1.358 (4)	1.344 (2)	1.326 (3)
C20—O21	1.251 (4)	1.216 (2)	1.224 (3)
C20—N22	1.355 (4)	1.402 (2)	1.392 (3)
N22—C23	1.348 (4)	1.349 (2)	1.358 (3)
C23—N24	1.324 (4)	1.311 (2)	1.314 (3)
C23—N25	1.338 (4)	1.325 (2)	1.319 (3)
N25—C26	-	1.432 (2)	-
O21···H24*A*	1.98 (4)	2.02 (2)	2.04 (3)
C13—N19—C20	-	128.72 (14)	-
N19—C20—N22	113.4 (3)	110.64 (13)	113.6 (2)
C20—N22—C23	119.8 (3)	126.91 (13)	125.9 (2)
N22—C23—N25	116.2 (3)	116.64 (13)	117.1 (2)
C23—N25—C26	-	125.78 (13)	-
O21—C20—N22	127.1 (3)	122.76 (14)	122.4 (2)
N22—C23—N24	126.3 (3)	120.96 (14)	121.0 (2)

Table 2. *Hydrogen-bonding geometry (Å, °)*

Mean *d*(N—H) = 0.88 Å; the e.s.d. of an individual measurement is 0.02 Å, and this is also the e.s.d. of the sample of six values. Note that the e.s.d.'s given in Table 3 of YHCT96 did not properly take into account the hydrogen e.s.d.'s.

N—H···O/N—C	*d*(N···O/N)	*d*(H···ON)	Angle †	Angle ‡
Intramolecular				
N24—H24*A*···O21=C20§	2.712 (2)	2.02 (2)	134 (2)	98.3 (6)
Cation-to-anion				
N19—H19···N12≡C11	2.888 (2)	2.01 (2)	166 (2)	134.7 (5)
N22—H22···N12≡C11	2.943 (2)	2.16 (2)	157 (2)	103.6 (5)
N24—H24*B*···N12^{i}≡C11^{i}	2.979 (2)	2.20 (2)	147 (2)	114.6 (5)
N24–H24*A*···O21^{ii}=C20^{ii}§	3.037 (2)	2.38 (2)	134 (2)	152.2 (5)
N25—H25···O9=C8	2.813 (2)	1.96 (2)	163 (2)	144.9 (5)
Anion-to-anion				
N7—H7···N10^{iii}—C8^{iii}	3.063 (2)	2.26 (2)	177 (2)	134.9 (5)

† N—H···O/N. ‡ H···O/N—C. § Bifurcated hydrogen bond formed by N24—H24*A*.

Symmetry codes: (i) $1+x, y, z$; (ii) $1-x, -y, -z$; (iii) $-x, 1-y, 1-z$.

Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP*II (Johnson, 1976).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1255). Services for accessing these data are described at the back of the journal.

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***trans*-Methyl 2,9-Bis(phenylsulfonyl)-1,2,3,4-tetrahydro-4-β-carbolinylidene-acetate†**

E. Subramanian,* L. Govindasamy and K. Ravichandran

Department of Crystallography and Biophysics, University of Madras, Guindy Campus, Madras 600 025, India. E-mail: crystal@giasmd01.vsnl.net.in

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Abstract

The title compound, $C_{26}H_{22}N_2O_6S_2$, consists of a β-carboline moiety, two phenylsulfonyl groups and one methoxycarbonylmethylene group. The six-membered heterocyclic ring adopts a half-chair conformation. The substituent at the indole N atom is equatorial while that at the second N atom is axial. The methoxycarbonylmethylene group is approximately coplanar to the β-carboline moiety. The dihedral angle between the two phenyl rings is 78.3 (1)°.

Comment

Derivatives of β-carbolines have been used as inverse agonist pharmacophores for the benzodiazepine receptor. While 3-substituted β-carbolines have been shown to interact at benzodiazepine receptors, a number of other related β-carbolines have proven to be effective non-competitive inhibitors of the indolamine 2,3-dioxygenase (IDO) enzyme system (Cox & Cook, 1995). The tetrahydro-β-carboline unit is central to an enormous range of indole alkaloids, and stereospecific syntheses of derivatives are widely sought (Everett *et al.*, 1990).

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† DCB contribution No. 877.