

Fig. 3. Crystal packing of CB viewed (a) along *a*; (b) along the crystallographic *c* axis.

The molecules of CB pack together with a quasi-parallel orientation of the elongation axes but, at variance with CA, a large molecular intercalation occurs along that direction and no layers are formed (Fig. 3a). A view of the crystal packing along the crystallographic *c* axis is shown in Fig. 3(b) giving evidence of the packing differences with respect to CA.

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### Structure of 3-Benzoyl-1,1,2-tricyano-3-(1-pyridinio)-2-propen-1-ide

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**Abstract.**  $C_{18}H_{10}N_4O$ ,  $M_r = 298$ , monoclinic,  $P2_1/c$ ,  $a = 9.8958$  (8),  $b = 15.3406$  (19),  $c = 10.5753$  (11) Å,  $\beta = 111.803$  (7)°,  $V = 1490.6$  (3) Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.329$ ,  $D_m = 1.315$  g cm<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71069$  Å,  $\mu = 2.027$  cm<sup>-1</sup>,  $F(000) = 616$ ,  $T = 293$  K. The structure was solved by direct methods and refined to  $R = 0.041$  for 1997 independent reflections. The negative charge is delocalized in the planar conjugated ylide fragment  $C(3)=C(2)-C(1)(CN)_2$  with the positive charge located on the N atom of the pyridinium ring. The planes of the  $Py^+$  and Ph substituents are rotated relative to the ylide plane by 107.5 and 60.9° respectively. Such orientation of the carbonyl group relative to the dicyanomethylide fragment, which is due to a number of shortened intramolecular contacts, is unfavourable for the cyclization of the compound studied.

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**Introduction.** The title compound (I) was obtained by the reaction of tetracyanoethylene with benzoylpyridiniummethylide; the latter is formed as a result of interaction of triethylamine with a methanol solution of *N*-phenylacetylpyridinium bromide. In contrast to the earlier-studied pyridinium ylides (Tominaga, Motokawa, Shiroshita & Hosomi, 1987), ylide (I) does not undergo, on heating, cyclization to the corresponding pyran or pyridine (depending on the reaction conditions).

An X-ray structural study of ylide (I) has been carried out in order to elucidate the peculiarities of its structure and the reasons for its inertness in cyclization.

**Experimental.** Prismatic ruby-coloured crystals were obtained on recrystallization of the salt (I) from ethanol. Density measured by flotation. One of the crystals, 0.3 × 0.3 × 0.4 mm in size, was used for the

X-ray study: the unit-cell parameters were determined (using setting angles for 12 reflections with  $14 < 2\theta < 16^\circ$ ) and intensities of 2738 independent reflections ( $-11 \leq h \leq 11$ ,  $0 \leq k \leq 18$ ,  $-10 \leq l \leq 10$ ) were measured with a four-circle automated Hilger & Watts diffractometer (293 K, Mo  $K\alpha$ , graphite monochromator,  $\theta/2\theta$  scan,  $2\theta_{\max} = 60^\circ$ ). The quality of the sample was monitored by measurements of intensities of two standard reflections after each 100 reflections, no intensity variation. No absorption or secondary-extinction corrections were applied. The structure was solved by direct methods with the *MULTAN* program package (Germain, Main & Woolfson, 1971), which allowed location of all non-hydrogen atoms, and was refined by a full-matrix least-squares techniques in the anisotropic approximation for non-hydrogen atoms using 1997 independent reflections with  $I \geq 2\sigma$ . The minimized function was  $\sum w(|F_o| - |F_c|)^2$ ;  $w = [\sigma^2(F_c) + |0.03F_o|^2]^{-1}$ . Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV) were used. The hydrogen atoms were located in a difference Fourier synthesis and refined isotropically. The final discrepancy factors are  $R = 0.041$ ,  $wR = 0.052$ ,  $S = 2.34$ : the final value for the ratio (max. shift)/ $\sigma = 0.5$ : the maximum and the minimum peak heights of the final zero Fourier synthesis are  $\pm 0.4 \text{ e } \text{Å}^{-3}$ . All calculations were carried out with an Eclipse S/200 computer using the *INXTL* program package (Gerr, Yanovsky & Struchkov, 1983).

**Discussion.** Atomic coordinates and bond angles are listed in Tables 1 and 2 respectively. The structure of the molecule, (I), with the bond lengths is shown in Fig. 1.\*

The X-ray structural study confirmed that the compound is 3-benzoyl-1,1,2-tricyano-3-(1-pyridinio)-2-propen-1-ide. The molecule contains an approximately planar fragment, C(3), C(2), C(1), C(5), N(1), C(6) and N(2) [the plane *A*, deviations of the atoms from the plane do not exceed  $0.058(2) \text{ Å}$ ]. The ylide C(1) atom is in a planar trigonal  $sp^2$ -hybridized state (the sum of the bond angles is  $360^\circ$ ), its lone electron pair participates in conjugation with the double bond C(2)=C(3) and both nitrile groups bonded to the C(1) atom. Indeed, while the formally double C(2)=C(3) bond is elongated to  $1.384(3) \text{ Å}$  [the standard value for the C( $sp^2$ )=C( $sp^2$ ) bond is  $1.331 \text{ Å}$  (Allen, Kennard, Watson, Brammer, Orpen & Taylor, 1987)], the formally single bond C(1)—

Table 1. Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic temperature factors of atoms in structure (I)

$$U_{eq} = (1/3)\sum_i \sum_j B_{ij} a_i^* a_j^* a_i \cdot a_j$$

|       | x         | y        | z         | $B_{eq}(\text{Å}^2)$ |
|-------|-----------|----------|-----------|----------------------|
| O     | 1042 (2)  | 3241 (1) | 826 (1)   | 4.6 (1)              |
| N(1)  | 2924 (2)  | 4261 (2) | 6537 (2)  | 6.7 (1)              |
| N(2)  | -1475 (2) | 3911 (2) | 6245 (2)  | 7.0 (1)              |
| N(3)  | -2921 (2) | 3460 (1) | 2493 (2)  | 4.2 (1)              |
| N(4)  | 2265 (2)  | 3467 (1) | 3545 (1)  | 2.7 (1)              |
| C(1)  | 310 (2)   | 3874 (1) | 5011 (2)  | 2.9 (1)              |
| C(2)  | -137 (2)  | 3723 (1) | 3601 (2)  | 2.5 (1)              |
| C(3)  | 716 (2)   | 3624 (1) | 2829 (2)  | 2.7 (1)              |
| C(4)  | 259 (2)   | 3585 (1) | 1351 (2)  | 3.0 (1)              |
| C(5)  | 1760 (2)  | 4075 (1) | 5847 (2)  | 3.9 (1)              |
| C(6)  | -691 (2)  | 3879 (2) | 5675 (2)  | 4.1 (1)              |
| C(7)  | -1704 (2) | 3600 (1) | 2930 (2)  | 2.9 (1)              |
| C(8)  | 3232 (2)  | 4057 (1) | 3449 (2)  | 3.7 (1)              |
| C(9)  | 4689 (2)  | 3900 (2) | 4074 (2)  | 4.5 (1)              |
| C(10) | 5163 (2)  | 3156 (2) | 4816 (2)  | 4.6 (1)              |
| C(11) | 4165 (2)  | 2568 (1) | 4912 (2)  | 4.4 (1)              |
| C(12) | 2718 (2)  | 2726 (1) | 4261 (2)  | 3.6 (1)              |
| C(13) | -1152 (2) | 3993 (1) | 519 (2)   | 3.0 (1)              |
| C(14) | -2124 (2) | 3547 (1) | -592 (2)  | 4.3 (1)              |
| C(15) | -3474 (3) | 3905 (2) | -1320 (2) | 5.1 (1)              |
| C(16) | -3850 (2) | 4695 (2) | -980 (2)  | 4.8 (1)              |
| C(17) | -2872 (3) | 5158 (1) | 75 (2)    | 4.6 (1)              |
| C(18) | -1528 (2) | 4805 (1) | 825 (2)   | 3.6 (1)              |

Table 2. Bond angles ( $^\circ$ ) in structure (I)

|                 |           |                   |           |
|-----------------|-----------|-------------------|-----------|
| C(5)—C(1)—C(6)  | 115.1 (2) | C(3)—N(4)—C(12)   | 119.9 (2) |
| C(5)—C(1)—C(2)  | 123.1 (2) | C(8)—N(4)—C(12)   | 120.7 (2) |
| C(6)—C(1)—C(2)  | 121.7 (2) | N(4)—C(8)—C(9)    | 119.8 (2) |
| C(1)—C(2)—C(3)  | 128.5 (2) | C(8)—C(9)—C(10)   | 120.0 (2) |
| C(1)—C(2)—C(7)  | 113.3 (2) | C(9)—C(10)—C(11)  | 119.4 (2) |
| C(3)—C(2)—C(7)  | 118.1 (2) | C(10)—C(11)—C(12) | 119.9 (2) |
| C(2)—C(3)—C(4)  | 128.5 (2) | C(11)—C(12)—N(4)  | 120.2 (2) |
| C(2)—C(3)—N(4)  | 117.8 (2) | C(4)—C(13)—C(14)  | 119.8 (2) |
| N(4)—C(3)—C(4)  | 113.5 (2) | C(4)—C(13)—C(18)  | 121.4 (2) |
| C(3)—C(4)—O     | 120.4 (2) | C(14)—C(13)—C(18) | 118.8 (2) |
| C(3)—C(4)—C(13) | 117.9 (2) | C(13)—C(14)—C(15) | 119.8 (2) |
| O—C(4)—C(13)    | 121.7 (2) | C(14)—C(15)—C(16) | 120.7 (2) |
| C(1)—C(5)—N(1)  | 178.0 (2) | C(15)—C(16)—C(17) | 119.8 (2) |
| C(1)—C(6)—N(2)  | 177.2 (3) | C(16)—C(17)—C(18) | 120.2 (2) |
| C(2)—C(7)—N(3)  | 174.3 (2) | C(17)—C(18)—C(13) | 120.6 (2) |
| C(3)—N(4)—C(8)  | 119.3 (2) |                   |           |

C(2) is significantly shortened to  $1.408(2) \text{ Å}$  [the standard value for the length of the non-conjugated C( $sp^2$ )—C( $sp^2$ ) bond is  $1.478 \text{ Å}$  (Allen *et al.*, 1987)]. Similar values of bond lengths for the formally double and single bonds,  $1.364(5)$  and  $1.398(5) \text{ Å}$  respectively, were observed in the tetracyano-propenide anions of the salts of substituted hexahydrodibenzotriazolo[3,2-*a*]pyridinium (II) (Shestopalov, Nesterov, Sharanin, Litvinov, Mortikov, Shklover, Struchkov & Promonenkov, 1988) and triphenylpyrilium [(III),  $1.379(5)$  and  $1.388(5) \text{ Å}$  (Tamamura, Yamane, Yasuoka & Kasai, 1974)].

Participation of the CN groups in conjugation with the lone electron pair of the C(1) atom results on the one hand in the shortening of the C(1)—C(5) and C(1)—C(6) bonds to  $1.413(3)$  and  $1.411(3) \text{ Å}$  [the C(2)—C(7) bond length is  $1.458(3) \text{ Å}$ ; the standard value for the C( $sp^2$ )—C( $sp$ ), *e.g.* in TCNQ, is

\* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53065 (19 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

1.427 Å (Allen *et al.*, 1987)], and on the other hand in a slight elongation of the C≡N bond to 1.147 (3) Å [the C(7)≡N(3) bond length is 1.138 (3) Å: in TCNQ this value is 1.144 Å (Allen *et al.*, 1987)]. The C(sp<sup>2</sup>)—C(sp) and C≡N bonds in the tetracyanopropenide anions of the salts of (II) and (III) have the same lengths as in (I) and vary respectively in the following ranges: 1.415 (5)–1.430 (5) and 1.141 (5)–1.151 (5) Å [for (II) (Shestopalov *et al.*, 1988)], 1.408 (5)–1.422 (5) and 1.141 (5)–1.149 (5) Å [for (III) (Tamamura *et al.*, 1974)], which also indicate that cyano groups participate in charge delocalization. In the molecule of (1-pyridinium)di-cyanomethylide, which in contrast to (I) represents a 1,2-ylide, the lone electron pair of ylide carbon is conjugated only with cyano groups, which leads to a more pronounced redistribution of the bond lengths in this case than in (I) [C(sp<sup>2</sup>)—C(sp) 1.389 (1) and C≡N 1.158 (2) Å (Devos, Baert, Fourt & Thomas, 1980)]. Thus compound (I) is a 1,4-ylide with the negative charge delocalized between the three C atoms of the ylide moiety and the terminal CN groups.

The coordination plane of the C(4) atom [the *B* plane, with deviations from planarity not exceeding 0.009 (2) Å] is not coplanar with the above mentioned conjugated moiety *A* (the dihedral angle *A/B* is 142.5°), which might hinder further delocalization of electron density between the C(2)=C(3) and C(4)=O bonds. Nevertheless, the C(3)—C(4) bond of 1.458 (3) Å is somewhat shortened and the C(4)=O bond of 1.228 (3) Å is on the contrary slightly elongated [the standard C(sp<sup>2</sup>)—C(sp<sup>2</sup>) and C=O bond lengths are 1.478 and 1.199 Å respectively (Allen *et al.*, 1987)]. Consequently, it may be assumed that in spite of the non-coplanarity of the *A* and *B* moieties other slight conjugation may still exist.

The conformation of molecule (I) is a result of the compromise between the tendency to form a

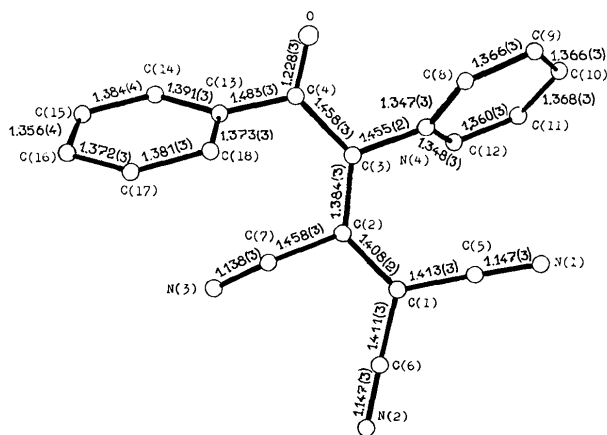


Fig. 1. General view of molecule (I), showing bond lengths (Å).

Table 3. Shortened non-bonded intramolecular contacts (Å) in structure (I)

The sums of the van der Waals radii of O and N, O and C, and N and C are 3.07, 3.22 and 3.25 Å respectively; the double van der Waals radius of carbon is 3.40 Å (Bondi, 1966).

|              |           |              |           |
|--------------|-----------|--------------|-----------|
| O...N(4)     | 2.696 (2) | C(3)...C(18) | 3.035 (3) |
| O...C(8)     | 3.081 (3) | C(4)...C(7)  | 2.995 (3) |
| O...C(14)    | 2.966 (3) | C(4)...C(8)  | 3.042 (3) |
| N(4)...C(1)  | 2.961 (2) | C(4)...C(12) | 3.402 (3) |
| N(4)...C(5)  | 2.820 (3) | C(5)...C(8)  | 3.361 (3) |
| C(1)...C(12) | 3.288 (3) | C(5)...C(12) | 3.029 (3) |
| C(2)...C(12) | 3.057 (3) | C(6)...C(7)  | 2.730 (3) |
| C(2)...C(13) | 3.061 (2) | C(7)...C(13) | 2.863 (3) |
| C(2)...C(18) | 3.205 (3) | C(7)...C(18) | 2.948 (3) |
| C(3)...C(5)  | 3.047 (3) |              |           |

common system of electron delocalization involving both *A* and *B* fragments on the one hand, and a considerable number of shortened non-bonded contacts on the other hand, between the Ph ring and the CN group at the C(2) atom, between the O atom of the carbonyl group and the pyridinium ring, as well as between the latter and the C(5)≡N(1) cyano group at the C(1) atom (Table 3). These contacts cause the rotation of the Py<sup>+</sup> and Ph substituents relative to the *A* plane by 107.5 and 60.9°, and relative to the *B* plane by 75.5 and 133.4°. Such large rotation angles prevent substituents from participating in conjugation with the *A* and *B* moieties. Indeed, the C(3)—N(4) bond length of 1.455 (2) Å significantly exceeds the standard value for the conjugated N(sp<sup>2</sup>)—C(sp<sup>2</sup>) bond [1.355 Å according to Allen *et al.* (1978)] and is close to the value characteristic of the single bond N<sup>+</sup>(sp<sup>2</sup>)—C(sp<sup>2</sup>) [e.g. 1.447 (8) and 1.448 (7) Å in *E* and *Z* isomers, coexisting in the crystal of 1-(2-amino-1-cyano-2-thioethylene)pyridinium ylide (Fischer, Knippel, Wollin, Kálmán & Argay, 1983)].

Moreover, the shortened intramolecular contacts lead to a considerable increase of the C(1)—C(2)—C(3) and C(2)—C(3)—C(4) bond angles to 128.5 (2) and 128.5 (2)°, while the C(1)—C(2)—C(7) [113.3 (2)°] and N(4)—C(3)—C(4) [113.5 (2)°] bond angles are considerably decreased [the steric Py<sup>+</sup>...O interaction is weaker than the Py<sup>+</sup>...C(5)≡N(1) interaction; Table 3].

The intermolecular contacts O...C(12') 3.119 (2) and O...H(12') 2.37 (2) Å [the C(12') and H(12') atoms are generated by the  $x, \frac{1}{2}-y, -\frac{1}{2}+z$  symmetry transformation] in the crystal of ylide (I) are somewhat shorter than the sum of the van der Waals radii of O and C or O and H atoms [3.22 and 2.72 Å (Bondi, 1966)].

In the conformation of molecule (I) found in the crystal, the C(4)=O carbonyl group has an orientation unfavourable for cyclization of (I) into a substituted pyran or pyridine (which demands the close approach of the oxygen atom and one of the nitrile

groups of the dicyanomethylidene moiety), viz this group is removed from the  $C(CN)_2$  moiety [the  $C(1)-C(2)-C(3)-C(4)$  and  $C(2)-C(3)-C(4)-O$  torsion angles are  $-170.9(3)$  and  $-157.8(3)^\circ$  respectively]. The conformation of molecule (I) in the crystal is fixed both by the extended conjugation system and by shortened non-bonded contacts. Thus a considerable change of conformation in solution seems quite improbable.

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## Structure of 4-(3-Chlorophenyl)thiosemicarbazide

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**Abstract.**  $C_7H_8ClN_3S$ ,  $M_r = 201.67$ , monoclinic,  $P2_1/c$ ,  $a = 6.914(5)$ ,  $b = 4.304(4)$ ,  $c = 30.306(3)$  Å,  $\beta = 94.66(3)^\circ$ ,  $V = 899.0(1)$  Å<sup>3</sup>,  $Z = 4$ ,  $D_m = 1.54$ ,  $D_x = 1.490$  Mg m<sup>-3</sup>,  $\lambda(Cu K\alpha) = 1.5418$  Å,  $\mu = 5.54$  mm<sup>-1</sup>,  $F(000) = 416$ ,  $T = 298$  K, final  $R = 0.048$  for 1219 observed reflections. The S and terminal hydrazinic N atoms are in a *trans* conformation. As a result of the  $\sigma$ -electron-withdrawing effect of the Cl atom at the *meta* position in the phenyl ring with respect to the thiosemicarbazide chain, the net negative charge on the terminal N atom decreases compared to the *p*-chloro and *p*-methoxy derivatives. The antibacterial activity of the compound is also lowered.

**Introduction.** The biological activities possessed by thiosemicarbazides and thiosemicarbazones arise from their reductive capacity and their ability to

form complexes with metal ions (Sorkin, Roth & Erlenmeyer, 1952; Kirschner, Wei, Francis & Bergman, 1966). Only the S and terminal hydrazinic N atoms are actively involved in binding the metal ions. Depending on the metal ion and the particular derivative of the ligand, one or both of these atoms can coordinate. Substituents at various points in the ligand framework alter the extent and the nature of biological activities of the product by virtue of their electronic effect, stereochemical effects, etc. Since the activity of these compounds is related to reductive and metal-chelating properties, substituents which improve the electron-donating capacity of the donor atoms, S and N(3), are expected to raise their activities. Nandi, Chaudhuri, Mazumdar & Ghosh (1984a) showed that the *in vitro* antibacterial activity of 4-(4-chlorophenyl)thiosemicarbazide increased significantly over that of 4-phenylthiosemicarbazide owing to electron enrichment in the thiosemicarbazide side chain caused by the presence of the Cl atom in the phenyl ring at a position *para* to the side

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