

terminal atom of the ethyl group appeared to be disordered and was refined over two sites with occupancies of 0.52 and 0.48. The occupancy factors were not refined in the final cycles as there were strong correlations with the position and displacement parameters of these atoms. All the partially occupied H atoms on the ethyl group were fixed on the basis geometrical estimates, while the other methyl H atoms were included at calculated positions and refined using a riding model, with a common isotropic displacement factor for each group. All other H atoms were refined with individual isotropic displacement factors.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, bond distances and angles involving non-H atoms and least-squares-planes data have been deposited with the IUCr (Reference: AS1118). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Diels–Alder Products of the Alkaloid (–)-Thebaine with α -Chloroacrylnitrile and 1-Methoxy-1,3-cyclohexadiene with Tetracyanoethene

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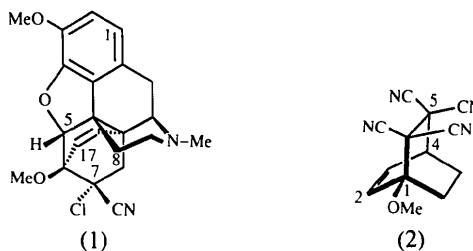
Abstract

(5*R*,6*S*,7*R*,9*R*,13*S*,14*R*)-7-Chloro-7-cyano-4,5-epoxy-3,6-dimethoxy-*N*-methyl-6,14-ethenoisomorphinan, (1), C₂₂H₂₃ClN₂O₃, and 1-methoxy-5,5,6,6-tetracyano-

bicyclo[2.2.2]oct-2-ene, (2), C₁₃H₁₀N₄O, which had not been convincingly characterized before by any other analytical method due to possible existence of several isomers, were obtained from the Diels–Alder reactions of (–)-thebaine [for compound (1)] and 1-methoxy-1,3-cyclohexadiene [for compound (2)]. The X-ray structural results provided reliable information on the stereochemical course of Diels–Alder reactions of (–)-thebaine and 1-methoxy-1,3-cyclohexadiene with α -chloroacrylnitrile and tetracyanoethene, respectively.

Comment

Diels–Alder reactions of the electron-rich opium alkaloid (–)-thebaine, as well as of related compounds also possessing 1,3-cyclohexadiene subunits, with acceptor-substituted dienophiles are of general interest in the development of new analgesic drugs (Bentley, 1954). The previously reported structural data on cycloadducts of thebaine and related systems (Bentley, 1971) is not completely convincing because of the possible existence of several stereoisomers. Therefore, reinvestigations of several Diels–Alder reactions of (–)-thebaine and related dienes, and detailed structural analysis of reaction products is still necessary (Pindur & Keilhofer, 1993; Pindur, Keilhofer & Schollmeyer, 1994) in order to carry out reliable studies on structure–activity relationships in medicinal chemistry.



The results of the X-ray structure determination of the title compounds (1) and (2) gave very detailed information concerning the course of the Diels–Alder reactions of (–)-thebaine with α -chloroacrylnitrile, and of 1-methoxy-1,3-cyclohexadiene, as a subunit model for thebaine, with tetracyanoethene. In the case of the [4 + 2] cycloaddition of (–)-thebaine with α -chloroacrylnitrile, a reliable determination of the configuration of the newly formed stereocentres was not possible previously (Pindur & Keilhofer, 1993) and has been the subject of some controversy (Hua, Jung, Ostrander & Takusagawa, 1987; Lewis, Readhead, Selby, Smith & Young, 1971). However, applications of several high-resolution NMR techniques were not able to clarify the regio- and stereochemistry of cycloadduct (1) (Pindur & Keilhofer, 1993) because of missing selective probes in the molecule to discriminate from eight different isomeric Diels–Alder products. We have now clarified unambiguously the

regio- and stereochemistries at the tetrahydrobarrele ring system in (1) by X-ray structure analysis.

The dienophile attacks the 1-methoxybutadiene ring system at (–)-thebaine from the sterically less-hindered site. In the case of the cycloadduct (2), the structural predictions made with the help of high-resolution NMR spectroscopy (Pindur & Keilhofer, 1993) have now been fully substantiated by the X-ray structure analysis. Alternative isomeric reaction products, for example a Michael-type adduct or rearrangement products, were ruled out emphatically.

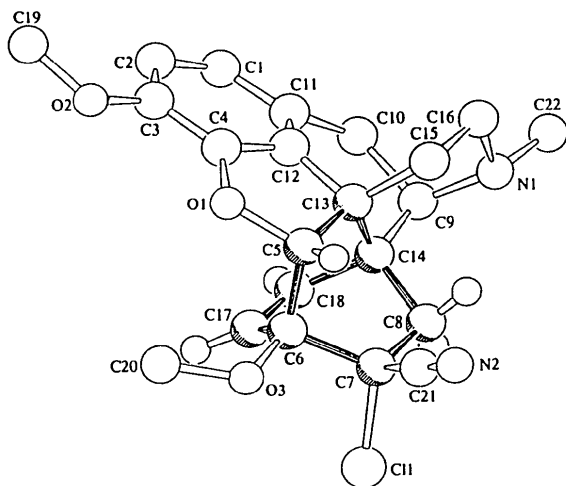


Fig. 1. SCHAKAL92 (Keller, 1992) plot for compound (1) with atomic numbering scheme. For clarity, only the most important H atoms are shown. The typical barrelene system is emphasized.

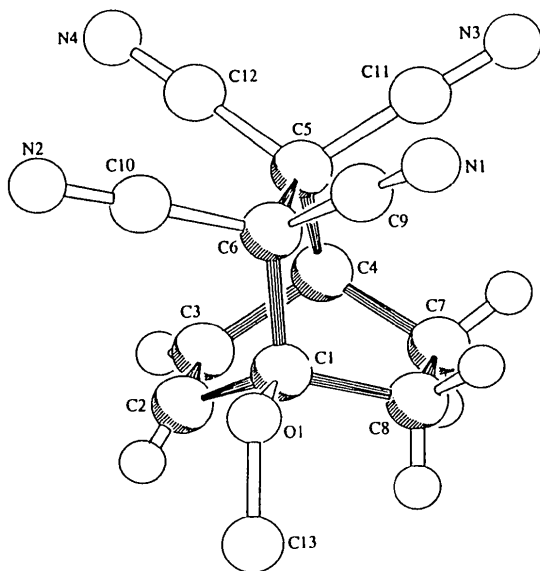


Fig. 2. SCHAKAL92 (Keller, 1992) plot for compound (2) with atomic numbering scheme. For clarity, only the most important H atoms are shown. The typical barrelene system is emphasized.

The barrelene fragments of (1) and (2) exhibit the same geometry. The three six-membered rings are in boat conformations which can be numerically described by puckering analysis (Cremer & Pople, 1975). The results of these calculations indicate near perfect C_3 symmetry with θ values of 87.5(2)–91.0(1)° (ideal value 90°).

Experimental

Crystals of compound (1) were formed by diffusion of petroleum ether into a solution of (1) in ethyl acetate. Crystals of (2) were obtained by slow evaporation of a chloroform solution.

Compound (1)

Crystal data

$C_{22}H_{23}ClN_2O_3$

$M_r = 398.87$

Triclinic

$P1$

$a = 6.7639(2) \text{ \AA}$

$b = 8.0105(1) \text{ \AA}$

$c = 9.3111(1) \text{ \AA}$

$\alpha = 95.703(1)^\circ$

$\beta = 106.774(1)^\circ$

$\gamma = 92.499(2)^\circ$

$V = 479.25(2) \text{ \AA}^3$

$Z = 1$

$D_x = 1.382 \text{ Mg m}^{-3}$

Cu $K\alpha$ radiation

$\lambda = 1.5418 \text{ \AA}$

Cell parameters from 75 reflections

$\theta = 32.5\text{--}35.5^\circ$

$\mu = 1.980 \text{ mm}^{-1}$

$T = 293(2) \text{ K}$

Prism

$0.51 \times 0.29 \times 0.26 \text{ mm}$

Light yellow

Data collection

Enraf–Nonius CAD-4

diffractometer

$\omega/2\theta$ scans

Absorption correction:

none

3803 measured reflections

3569 independent reflections

3558 observed reflections

$[I > 2\sigma(I)]$

$R_{\text{int}} = 0.0075$

$\theta_{\text{max}} = 69.85^\circ$

$h = -8 \rightarrow 8$

$k = -9 \rightarrow 9$

$l = -11 \rightarrow 11$

3 standard reflections

frequency: 60 min

intensity decay: 5%

Refinement

Refinement on F^2

$R[F^2 > 2\sigma(F^2)] = 0.0475$

$wR(F^2) = 0.1360$

$S = 1.126$

3569 reflections

267 parameters

Only H-atom U 's refined

$w = 1/[\sigma^2(F_o^2) + (0.0909P)^2$

$+ 0.1397P]$

where $P = (F_o^2 + 2F_c^2)$

$(\Delta/\sigma)_{\text{max}} = 0.020$

$\Delta\rho_{\text{max}} = 0.398 \text{ e \AA}^{-3}$

$\Delta\rho_{\text{min}} = -0.323 \text{ e \AA}^{-3}$

Extinction correction:

SHELXL93 (Sheldrick, 1993)

Extinction coefficient:

0.0217 (28)

Atomic scattering factors

from *International Tables*

for *Crystallography* (1992,

Vol. C, Tables 4.2.6.8 and

6.1.1.4)

Absolute configuration:

$\chi = 0.03(2)$ (Flack,

1983)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²) for (1)
$$U_{\text{eq}} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j.$$

	x	y	z	U_{eq}
C11	0.14986 (11)	0.45117 (9)	0.15887 (8)	0.0554 (2)
C1	0.5812 (5)	0.6211 (4)	1.0056 (3)	0.0485 (7)
C2	0.4441 (5)	0.7383 (4)	1.0310 (3)	0.0480 (7)
C3	0.2457 (4)	0.7417 (3)	0.9325 (3)	0.0400 (6)
C4	0.1890 (4)	0.6209 (3)	0.8088 (3)	0.0346 (5)
O1	0.0182 (3)	0.6169 (2)	0.6828 (2)	0.0397 (4)
C5	0.0408 (4)	0.4833 (3)	0.5710 (3)	0.0349 (5)
C6	0.0952 (4)	0.5502 (3)	0.4351 (3)	0.0359 (5)
C7	0.1092 (4)	0.3867 (3)	0.3288 (3)	0.0368 (5)
C8	0.2901 (4)	0.2833 (3)	0.4093 (3)	0.0372 (5)
C9	0.5614 (4)	0.2753 (3)	0.6710 (3)	0.0366 (5)
C10	0.6610 (4)	0.3791 (4)	0.8299 (3)	0.0413 (6)
C11	0.5184 (4)	0.4956 (3)	0.8850 (3)	0.0372 (5)
C12	0.3157 (4)	0.4945 (3)	0.7948 (3)	0.0334 (5)
C13	0.2200 (3)	0.3812 (3)	0.6523 (3)	0.0308 (5)
C14	0.3892 (4)	0.3694 (3)	0.5708 (3)	0.0322 (5)
C15	0.1419 (4)	0.2078 (3)	0.6793 (3)	0.0389 (6)
N1	0.4768 (4)	0.1036 (3)	0.6755 (3)	0.0412 (5)
C16	0.3206 (5)	0.1066 (3)	0.7561 (4)	0.0452 (6)
C17	0.3089 (4)	0.6381 (3)	0.4853 (3)	0.0387 (6)
C18	0.4585 (4)	0.5470 (3)	0.5544 (3)	0.0364 (5)
O2	0.1058 (4)	0.8581 (3)	0.9446 (3)	0.0530 (5)
C19	0.1517 (8)	0.9652 (6)	1.0814 (5)	0.0798 (14)
O3	-0.0629 (3)	0.6378 (2)	0.3479 (2)	0.0497 (5)
C20	-0.0909 (6)	0.8015 (4)	0.4090 (4)	0.0595 (9)
C21	-0.0916 (5)	0.2849 (4)	0.2792 (3)	0.0457 (6)
N2	-0.2399 (5)	0.2025 (4)	0.2458 (4)	0.0678 (9)
C22	0.6392 (5)	-0.0062 (4)	0.7404 (4)	0.0548 (8)

C6—C7—C11	108.3 (2)	C18—C17—C6	115.2 (2)
C14—C8—C7	108.5 (2)	C17—C18—C14	115.2 (2)
N1—C9—C14	108.7 (2)	C3—O2—C19	117.0 (3)
N1—C9—C10	114.8 (2)	C6—O3—C20	117.6 (2)
C14—C9—C10	111.1 (2)	N2—C21—C7	176.8 (4)
C11—C10—C9	115.3 (2)		
C6—C7—C8—C14	3.2 (2)	C6—C17—C18—C14	0.2 (3)
C6—C5—C13—C14	-2.9 (2)	C13—C5—C6—C17	-51.0 (3)

Compound (2)

Crystal data

C₁₃H₁₀N₄O $M_r = 238.25$

Orthorhombic

 $P2_1 2_1 2_1$ $a = 7.5252 (5) \text{ \AA}$ $b = 9.398 (1) \text{ \AA}$ $c = 17.2900 (7) \text{ \AA}$ $V = 1222.8 (2) \text{ \AA}^3$ $Z = 4$ $D_x = 1.294 \text{ Mg m}^{-3}$

Data collection

Enraf-Nonius CAD-4

diffractometer

 $\omega/2\theta$ scans

Absorption correction:

none

2648 measured reflections

2277 independent reflections

2218 observed reflections

 $|I| > 2\sigma(I)$

Refinement

Refinement on F^2 $R[F^2 > 2\sigma(F^2)] = 0.0527$ $wR(F^2) = 0.1407$ $S = 1.031$

2277 reflections

171 parameters

Only H-atom U 's refined $w = 1/[\sigma^2(F_o^2) + (0.1125P)^2$ $+ 0.1044P]$ where $P = (F_o^2 + 2F_c^2)/3$ $(\Delta/\sigma)_{\text{max}} = -0.003$ $\Delta\rho_{\text{max}} = 0.225 \text{ e \AA}^{-3}$ $\Delta\rho_{\text{min}} = -0.168 \text{ e \AA}^{-3}$ Table 3. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²) for (2)

$$U_{\text{eq}} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j.$$

Table 2. Selected geometric parameters (Å, °) for (1)

C11—C7	1.802 (3)	C9—N1	1.476 (3)
C1—C11	1.384 (4)	C9—C14	1.544 (3)
C1—C2	1.398 (5)	C9—C10	1.570 (4)
C2—C3	1.393 (4)	C10—C11	1.527 (4)
C3—O2	1.376 (3)	C11—C12	1.385 (4)
C3—C4	1.380 (4)	C12—C13	1.489 (3)
C4—C12	1.375 (4)	C13—C15	1.535 (3)
C4—O1	1.385 (3)	C13—C14	1.546 (3)
O1—C5	1.461 (3)	C14—C18	1.515 (3)
C5—C13	1.546 (3)	C15—C16	1.527 (4)
C5—C6	1.552 (4)	N1—C16	1.461 (4)
C6—O3	1.405 (3)	N1—C22	1.467 (4)
C6—C17	1.503 (4)	C17—C18	1.324 (4)
C6—C7	1.585 (3)	O2—C19	1.409 (4)
C7—C21	1.480 (4)	O3—C20	1.419 (4)
C7—C8	1.558 (4)	C21—N2	1.123 (5)
C8—C14	1.536 (3)		
C11—C1—C2	120.5 (3)	C12—C11—C1	116.0 (2)
C3—C2—C1	122.3 (3)	C12—C11—C10	117.8 (2)
O2—C3—C4	117.5 (2)	C1—C11—C10	125.4 (2)
O2—C3—C2	126.0 (2)	C4—C12—C11	123.3 (2)
C4—C3—C2	116.4 (2)	C4—C12—C13	110.0 (2)
C12—C4—C3	120.5 (2)	C11—C12—C13	125.4 (2)
C12—C4—O1	112.4 (2)	C12—C13—C15	113.0 (2)
C3—C4—O1	126.9 (2)	C12—C13—C14	105.4 (2)
C4—O1—C5	107.3 (2)	C15—C13—C14	112.2 (2)
O1—C5—C13	107.0 (2)	C12—C13—C5	101.4 (2)
O1—C5—C6	113.4 (2)	C15—C13—C5	112.1 (2)
C13—C5—C6	108.1 (2)	C14—C13—C5	112.0 (2)
O3—C6—C17	116.3 (2)	C18—C14—C8	105.8 (2)
O3—C6—C5	113.0 (2)	C18—C14—C9	113.8 (2)
C17—C6—C5	110.5 (2)	C8—C14—C9	115.3 (2)
O3—C6—C7	105.6 (2)	C18—C14—C13	107.6 (2)
C17—C6—C7	105.5 (2)	C8—C14—C13	108.5 (2)
C5—C6—C7	104.9 (2)	C9—C14—C13	105.5 (2)
C21—C7—C8	111.8 (2)	C16—C15—C13	111.6 (2)
C21—C7—C6	110.1 (2)	C16—N1—C9	110.8 (3)
C8—C7—C6	110.8 (2)	C16—N1—C9	111.2 (2)
C21—C7—C11	105.5 (2)	C22—N1—C9	112.3 (2)
C8—C7—C11	110.1 (2)	N1—C16—C15	110.6 (2)

	x	y	z	U_{eq}
C1	0.1974 (3)	0.3606 (2)	0.87082 (10)	0.0474 (4)
C2	0.2124 (3)	0.3842 (2)	0.78435 (11)	0.0530 (5)
C3	0.3525 (3)	0.4664 (3)	0.76335 (11)	0.0581 (6)
C4	0.4660 (3)	0.5150 (3)	0.83029 (11)	0.0526 (5)
C5	0.3425 (2)	0.6074 (2)	0.88505 (10)	0.0431 (4)
C6	0.1732 (2)	0.5136 (2)	0.90747 (9)	0.0391 (4)
C7	0.5264 (3)	0.3858 (3)	0.87587 (14)	0.0645 (6)
C8	0.3714 (4)	0.2977 (3)	0.90137 (13)	0.0641 (6)
C9	0.1501 (2)	0.4995 (2)	0.99205 (10)	0.0462 (4)
N1	0.1305 (3)	0.4860 (2)	1.05666 (9)	0.0663 (5)
C10	0.0086 (2)	0.5750 (2)	0.87629 (11)	0.0469 (4)
N2	-0.1193 (3)	0.6204 (3)	0.84990 (13)	0.0679 (6)

Cu $K\alpha$ radiation $\lambda = 1.5418 \text{ \AA}$

Cell parameters from 74

reflections

 $\theta = 32.5\text{--}35.0^\circ$ $\mu = 0.710 \text{ mm}^{-1}$ $T = 293 (2) \text{ K}$

Rectangular

 $1.09 \times 0.49 \times 0.33 \text{ mm}$

Reddish

 $R_{\text{int}} = 0.0690$ $\theta_{\text{max}} = 69.90^\circ$ $h = -8 \rightarrow 9$ $k = -11 \rightarrow 11$ $l = -20 \rightarrow 20$

3 standard reflections

frequency: 60 min

intensity decay: 5%

Extinction correction:

SHELXL93 (Sheldrick, 1993)

Extinction coefficient:

0.0038 (14)

Atomic scattering factors

from *International Tables*for *Crystallography* (1992,

Vol. C, Tables 4.2.6.8 and

6.1.1.4)

Absolute configuration:

 $\chi = 0.4 (4)$ (Flack, 1983)

C11	0.4473 (3)	0.6496 (2)	0.95378 (11)	0.0526 (5)
N3	0.5372 (3)	0.6799 (2)	1.00374 (12)	0.0703 (6)
C12	0.2915 (3)	0.7386 (2)	0.84392 (11)	0.0528 (5)
N4	0.2583 (3)	0.8366 (3)	0.80851 (13)	0.0762 (7)
O1	0.0429 (3)	0.2866 (2)	0.89409 (10)	0.0640 (5)
C13	0.0279 (6)	0.1443 (3)	0.8664 (2)	0.0957 (12)

Table 4. Selected geometric parameters (\AA , $^\circ$) for (2)

C1—O1	1.414 (3)	C5—C6	1.597 (2)
C1—C2	1.516 (3)	C6—C10	1.468 (3)
C1—C8	1.531 (3)	C6—C9	1.479 (2)
C1—C6	1.582 (3)	C7—C8	1.497 (4)
C2—C3	1.356 (3)	C9—N1	1.134 (2)
C3—C4	1.509 (3)	C10—N2	1.148 (3)
C4—C7	1.518 (3)	C11—N3	1.133 (3)
C4—C5	1.585 (3)	C12—N4	1.133 (3)
C5—C12	1.475 (3)	O1—C13	1.425 (3)
C5—C11	1.481 (3)		
O1—C1—C2	114.5 (2)	C11—C5—C6	112.22 (14)
O1—C1—C8	114.5 (2)	C4—C5—C6	108.09 (15)
C2—C1—C8	109.5 (2)	C10—C6—C9	107.42 (15)
O1—C1—C6	103.79 (14)	C10—C6—C1	107.89 (15)
C2—C1—C6	105.7 (2)	C9—C6—C1	109.16 (15)
C8—C1—C6	108.2 (2)	C10—C6—C5	111.53 (15)
C3—C2—C1	113.9 (2)	C9—C6—C5	112.52 (14)
C2—C3—C4	114.0 (2)	C1—C6—C5	108.20 (14)
C3—C4—C7	109.0 (2)	C8—C7—C4	111.2 (2)
C3—C4—C5	107.0 (2)	C7—C8—C1	110.6 (2)
C7—C4—C5	107.7 (2)	N1—C9—C6	178.5 (2)
C12—C5—C11	107.6 (2)	N2—C10—C6	177.9 (2)
C12—C5—C4	108.8 (2)	N3—C11—C5	175.6 (3)
C11—C5—C4	108.3 (2)	N4—C12—C5	175.7 (2)
C12—C5—C6	111.77 (15)	C1—O1—C13	115.6 (2)
C1—C2—C3—C4	1.0 (2)	C4—C5—C6—C1	3.3 (2)
C4—C7—C8—C1	2.5 (2)	C2—C1—C6—C5	-59.5 (2)

For both compounds, data collection: Enraf–Nonius CAD-4 software; cell refinement: *CELSIUS* (local software); data reduction: *CORINC* (local software); program(s) used to solve structures: *SHELXS86* (Sheldrick, 1990); program(s) used to refine structures: *SHELXL93* (Sheldrick, 1993); molecular graphics: *SCHAKAL92* (Keller, 1992); software used to prepare material for publication: *SHELXL93*.

We wish to thank the Deutsche Forschungsgemeinschaft, Bonn, for financial support.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: SE1061). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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*N*²-Cyano-*N*¹-isopropyl-*N*³-[4-(3-methylphenylamino)-3-pyridylsulfonyl]guanidine

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Abstract

The title compound, $\text{C}_{17}\text{H}_{20}\text{N}_6\text{O}_2\text{S}$, is a bioisoster of torasemide, a loop diuretic whose structure has been described previously. The sulfonylurea chain of torasemide is replaced by a sulfonylcyanoguanidine function. Whereas the torasemide molecule and some sulfonylurea derivatives exhibit one of the three α , β or γ conformations, the conformation being assigned according to the torsion angles in the side chain, the title compound displays a new δ conformation. This conformation is stabilized by two intramolecular $\text{N—H}\cdots\text{O}$ hydrogen bonds. A prototropic form of the title compound corresponding to a zwitterion [$-\text{S—N}^-\text{—C—}$, $\text{N}^+\text{—H}$ (pyridinium)] is observed {*i.e.* *N*²-cyano-*N*¹-isopropyl-*N*³-[4-(3-methylphenylamino)-3-pyridiniosulfonyl]guanidin-3-ide}. The crystal cohesion is the result of both van der Waals interactions and one intermolecular $\text{N}^+\text{—H}\cdots\text{N}^-$ hydrogen bond involving the N atoms of the zwitterion.

Comment

*N*²-Cyano-*N*¹-isopropyl-*N*³-[4-(3-methylphenylamino)-3-pyridylsulfonyl]guanidine, (I), is a bioisoster of torasemide, a loop diuretic (Friedel & Buckley, 1991) whose structure has been described previously (Dupont, Campsteyn, Lamotte & Vermeire, 1978; Dupont, Lamotte, Campsteyn & Vermeire, 1978). The structure differs from that of torasemide in that the sulfonylurea side