

Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1307). Services for accessing these data are described at the back of the journal.

## References

- Bochringer, C. F. & Soehne, G. M. B. H. (1961). *Chem. Abstr.* **55**, 24796.  
 Ganellin, C. R. & Spickett, R. G. W. (1965). *J. Med. Chem.* **8**, 619–625.  
 Mobio, I. G., Soldatenkov, A. T., Fedorov, V. O., Ageev, E. A., Sargeeva, N. D., Lin, S., Stashenko, E. E., Prostakov, N. S. & Andreeva, E. I. (1990). *Khim. Farm. Zh. Chem. Abstr.* **112**, 7331y.  
 Nardelli, M. (1983). *Comput. Chem.* **7**, 95–98.  
 Nardelli, M. (1995). *J. Appl. Cryst.* **28**, 659.  
 Nardelli, M. (1997). *CYLABS. Program for Cylindrical Absorption Correction*. University of Parma, Italy.  
 Ravindran, T., Jeyaraman, R., Murray, R. W. & Singh, M. (1991). *J. Org. Chem.* **56**, 4833–4840.  
 Robinson, O. P. W. (1973). *Post-Grad. Med. J.* **49** (Suppl.), 9–12.  
 Severs, W. B., Kinnard, W. J. & Buckley, J. P. (1965). *Chem. Abstr.* **63**, 10538.  
 Sheldrick, G. M. (1990). *Acta Cryst.* **A46**, 467–473.  
 Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.  
 Siemens (1992). *XSCANS Users Manual*. Version 2.0. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.  
 Zsolnai, L. (1997). *ZORTEP. Program for Crystal Structure Illustration*. University of Heidelberg, Germany.

*Acta Cryst.* (1998). **C54**, 872–875

## Three Cycloadducts Formed by the Reaction of Bis(phenylazo)stilbene with Acetylenic and Olefinic Dipolarophiles

D. RAMAIAH,<sup>a</sup> NIGAM P. RATH<sup>b</sup> AND M. V. GEORGE<sup>a,c,d</sup>

<sup>a</sup>Photochemistry Research Unit, Regional Research Laboratory (CSIR), Trivandrum 695 019, India, <sup>b</sup>Department of Chemistry, University of Missouri–St Louis, 8001 Natural Bridge Road, St Louis, MO 63121, USA, <sup>c</sup>Radiation Laboratory, University of Notre Dame, Notre Dame, IN 46556, USA, and <sup>d</sup>Jawaharlal Nehru Center for Advanced Scientific Research, Bangalore 560 064, India. E-mail: nigam\_rath@umsl.edu

(Received 16 June 1997; accepted 19 November 1997)

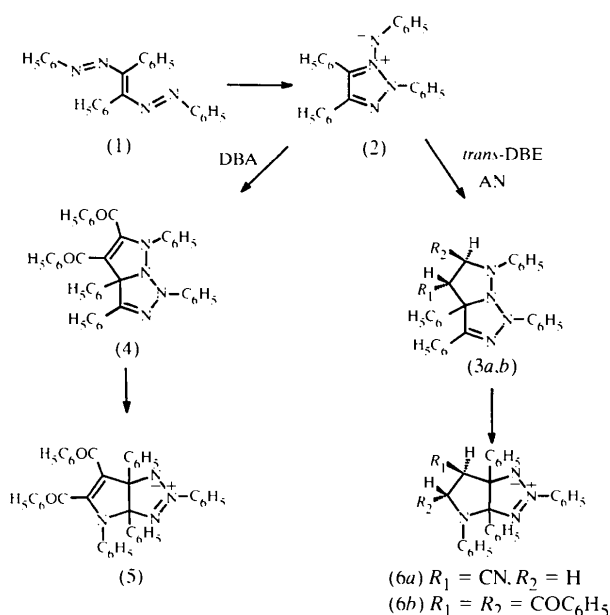
### Abstract

Bis(phenylazo)stilbene, (1), undergoes facile cycloaddition reactions with acetylenic and olefinic dipolarophiles to give the corresponding cycloadducts. The cycloadducts of (1) with dibenzoylacetylene (DBA), *trans*-1,2-dibenzoyl ethylene (*trans*-DBE) and acrylonitrile (AN) have been unambiguously identified through X-ray crystallographic analysis as, formally, 5,6-dibenzoyl-2,3a,4,6a-tetrahydro-1,2,3,4-tetraazapentalene [(5)], 2,3a,4,6a-tetrahydro-1,2,3,4-tetraazapentalene-6-carbonitrile [(6a)] and 5,6-dibenzoyl-2,3a,4,6a-tetrahydro-1,2,3,4-tetraazapentalene [(6b)], in each of which there is a delocalized double bond over atoms N1, N2 and N3 [N1 $\cdots$ N2 $\cdots$ N3: N1 $\cdots$ N2/N2 $\cdots$ N3 1.297 (2)/1.305 (2), 1.308 (2)/1.302 (1) and 1.298 (1)/1.298 (1) Å for (5), (6a) and (6b), respectively]. In (5), the C(O)C<sub>6</sub>H<sub>5</sub> substituent on C6 is almost fully conjugated with the C5=C6 double bond [O2=C3—C6=C5 torsion angle 166.4 (2)°]. Compounds (5), (6a) and (6b) are examples of a new class of heterocyclic compounds.

1,2,3,4-tetraazapentalene [C<sub>42</sub>H<sub>30</sub>N<sub>4</sub>O<sub>2</sub>, (5)], 2,3a,4,6a-tetrahydro-1,2,3,4-tetraazapentalene-6-carbonitrile [C<sub>29</sub>H<sub>23</sub>N<sub>5</sub>, (6a)] and 5,6-dibenzoyl-2,3a,4,6a-tetrahydro-1,2,3,4-tetraazapentalene [C<sub>42</sub>H<sub>32</sub>N<sub>4</sub>O<sub>2</sub>, (6b)], in each of which there is a delocalized double bond over atoms N1, N2 and N3 [N1 $\cdots$ N2 $\cdots$ N3: N1 $\cdots$ N2/N2 $\cdots$ N3 1.297 (2)/1.305 (2), 1.308 (2)/1.302 (1) and 1.298 (1)/1.298 (1) Å for (5), (6a) and (6b), respectively]. In (5), the C(O)C<sub>6</sub>H<sub>5</sub> substituent on C6 is almost fully conjugated with the C5=C6 double bond [O2=C3—C6=C5 torsion angle 166.4 (2)°]. Compounds (5), (6a) and (6b) are examples of a new class of heterocyclic compounds.

### Comment

Several suggestions have been made concerning the structures of the oxidation products of bisphenylhydrazones and bisbenzoylhydrazones of 1,2-diketones. These include a dihydro-1,2,3,4-tetrazine structure (von Pechman, 1897) and a bisazoolefin structure (Stolle, 1926; Grammaticakis, 1947) for the oxidation products of 1,2-diketone bisphenylhydrazones, whereas enol derivatives have been suggested as the oxidation products of bisbenzoylhydrazones of 1,2-diketones (Curtin & Alexandrou, 1963). A suggestion has also been made (Bauer *et al.*, 1964) that certain *ortho*-bisazo compounds containing electron-withdrawing groups attached to one of the azo groups exist in the meso-ionic form. It has been reported (Angadiyavar *et al.*, 1971; Sukumar *et al.*, 1972) that the oxidation products of bisphenylhydrazones of several 1,2-diketones undergo facile 1,3-dipolar cycloaddition reactions with acetylenic and olefinic dipolarophiles to give adducts such as (4), (3a) and (3b).



In view of the unusual structural features of these adducts, it was felt necessary to verify these structures through single-crystal X-ray analysis.

Preliminary X-ray analysis of (1) confirmed the structure as the open form of the bis(phenylazo)alkene with *trans* geometry. However, we were unable to obtain crystals that could yield publication-quality data (Ramaiah *et al.*, 1997). By contrast, the structures of the representative cycloadducts of (1) with DBA, *trans*-DBE and AN were found to be the unusual rearrangement products (5), (6a) and (6b), respectively, instead of the earlier proposed structures (4), (3a) and (3b).

Compounds (5) and (6a) crystallize in the triclinic space group  $P\bar{1}$ , while (6b) crystallizes in the monoclinic space group  $P2_1/n$ . All three compounds contain the interesting tetraazapentalene skeleton and are examples of a new class of heterocyclic compounds. The bicyclic tetraazapentalene framework has bridgehead atoms C3a and C6a substituted by phenyl groups. The 'butterfly angle' formed by the intersection of the two almost planar five-membered rings is  $67.71(4)^\circ$  in (5),  $64.58(3)^\circ$  in (6a) and  $76.11(4)^\circ$  in (6b).

Though the structures may be represented as having localized bonding  $N1-N2=N3$ , the bond distances indicate delocalization of the double bond. The  $N1=N2$  and  $N2=N3$  distances are equivalent to each other within experimental error [ $N1=N2/N2=N3$  1.297(2)/1.305(2), 1.308(2)/1.302(1) and 1.298(1)/1.298(1) Å;  $N1=N2=N3$  123.8(1), 123.0(1) and  $123.2(1)^\circ$ , for (5), (6a) and (6b), respectively].

In (5), the  $C(O)C_6H_5$  substituent on C6 is almost fully conjugated with the  $C5=C6$  double bond [ $O2=C32-$

$C6=C5$   $166.4(2)^\circ$ , which is a measure of the degree of conjugation according to Jones *et al.* (1995)]. However, the  $C(O)C_6H_5$  substituent on C5 is rotated away from the plane [ $O1=C25-C5=C6$   $112.1(3)^\circ$ ], indicating 14% conjugation.

The largest deviation from the tetrahedral angle at the bridgehead positions is observed at C3a in compound (6a) [ $N3-C3a-N4$   $109.1(1)$ ,  $113.8(1)$  and  $109.6(1)^\circ$ ;  $N1-C6a-C6$   $110.3(1)$ ,  $107.6(1)$  and  $106.8(1)^\circ$ , in (5), (6a) and (6b), respectively].

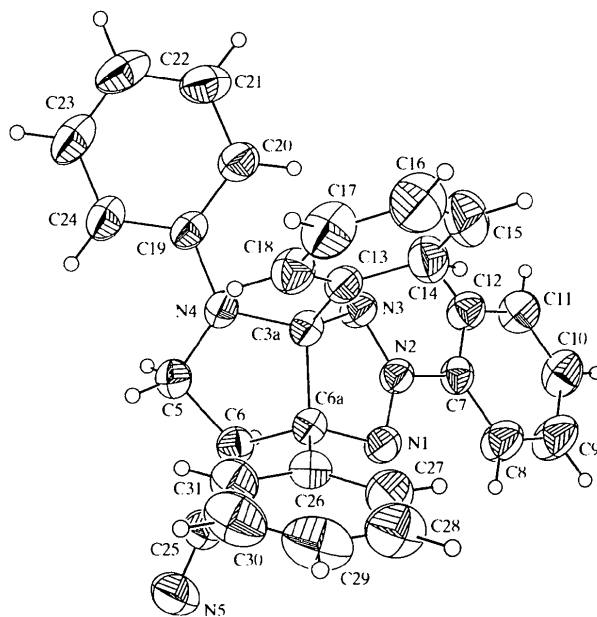


Fig. 2. View of a molecule of (6a) with 50% probability ellipsoids.

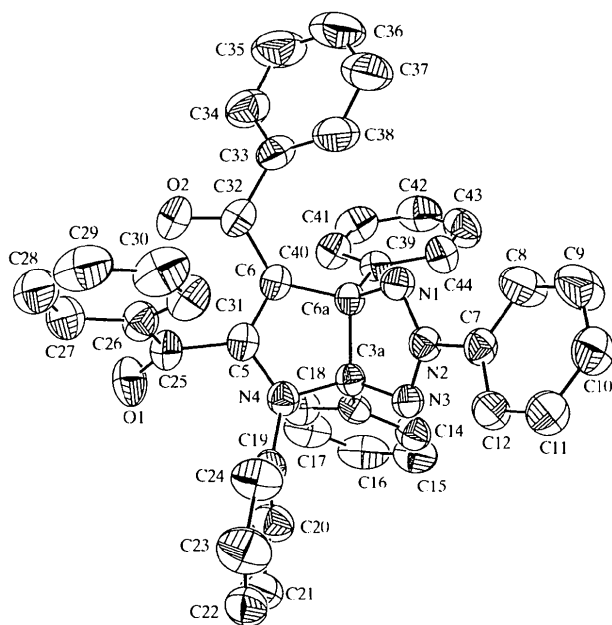


Fig. 1. View of a molecule of (5) with 50% probability ellipsoids.

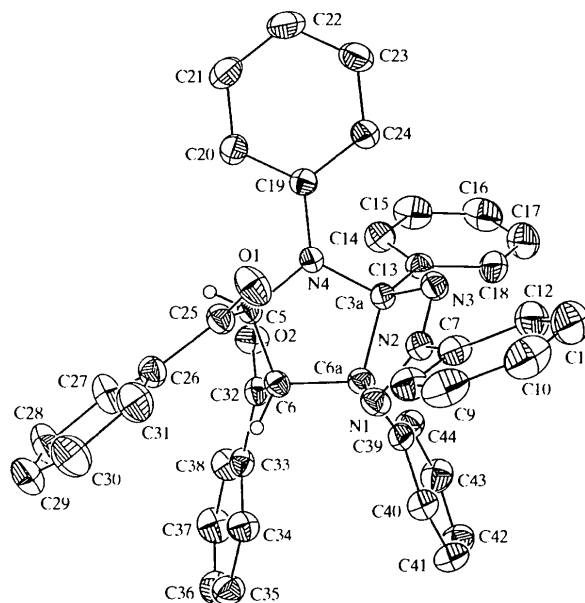


Fig. 3. View of a molecule of (6b) with 50% probability ellipsoids.

In (6a), the N atom of the carbonitrile group is involved in a long-range intermolecular interaction with a H atom attached to C5 [H5B...N5<sup>1</sup> 2.610 Å and C5—H5B...N5<sup>1</sup> 161.6°; symmetry code: (i)  $-x-1, 1-y, -z$ ].

In (6b), the torsion angle C25—C5—C6—C32 is 141.8(1)°, indicating a *trans* geometry for the two benzoyl substituents. The H atoms connected to C5 and C6 were located and refined in order to confirm the *trans* configuration. It is therefore evident that the cycloaddition of (1) to *trans*-DBE proceeds in a stereospecific manner, leading to the *trans*-adduct (6b).

All bond angles and distances are within the accepted ranges. No unusual intermolecular non-bonded contacts were observed in the crystal lattices.

## Experimental

Compounds (5), (6a) and (6b) were prepared according to the procedures described by Sukumaran *et al.* (1972). Diffraction-quality crystals were mounted on glass fibres in random orientations.

### Compound (5)

#### Crystal data

C <sub>42</sub> H <sub>30</sub> N <sub>4</sub> O <sub>2</sub>	Mo K $\alpha$ radiation
$M_r = 622.70$	$\lambda = 0.71073 \text{ \AA}$
Triclinic	Cell parameters from 8192 reflections
$P\bar{1}$	$\theta = 2.0\text{--}23.7^\circ$
$a = 10.6443 (1) \text{ \AA}$	$\mu = 0.079 \text{ mm}^{-1}$
$b = 10.9621 (1) \text{ \AA}$	$T = 298 (2) \text{ K}$
$c = 16.1129 (2) \text{ \AA}$	Prism
$\alpha = 86.010 (1)^\circ$	$0.45 \times 0.33 \times 0.25 \text{ mm}$
$\beta = 81.937 (1)^\circ$	Yellow
$\gamma = 61.998 (1)^\circ$	
$V = 1643.59 (3) \text{ \AA}^3$	
$Z = 2$	
$D_x = 1.258 \text{ Mg m}^{-3}$	
$D_m$ not measured	

#### Data collection

Siemens CCD diffractometer	$R_{\text{int}} = 0.031$
$\omega$ scans	$\theta_{\text{max}} = 28^\circ$
Absorption correction: none	$h = -14 \rightarrow 14$
15 512 measured reflections	$k = -15 \rightarrow 15$
7891 independent reflections	$l = -21 \rightarrow 22$
5237 reflections with $I > 2\sigma(I)$	

#### Refinement

Refinement on $F^2$	$(\Delta/\sigma)_{\text{max}} = 0.001$
$R[F^2 > 2\sigma(F^2)] = 0.047$	$\Delta\rho_{\text{max}} = 0.160 \text{ e \AA}^{-3}$
$wR(F^2) = 0.129$	$\Delta\rho_{\text{min}} = -0.206 \text{ e \AA}^{-3}$
$S = 1.032$	Extinction correction: none
7868 reflections	Scattering factors from <i>International Tables for Crystallography</i> (Vol. C)
433 parameters	
H atoms not refined	
$w = 1/[\sigma^2(F_o^2) + (0.0628P)^2 + 0.11P]$	
where $P = (F_o^2 + 2F_c^2)/3$	

### Compound (6a)

#### Crystal data

C <sub>29</sub> H <sub>23</sub> N <sub>5</sub>	Mo K $\alpha$ radiation
$M_r = 441.52$	$\lambda = 0.71073 \text{ \AA}$
Triclinic	Cell parameters from 7825 reflections
$P\bar{1}$	$\theta = 2.0\text{--}22.5^\circ$
$a = 9.2081 (1) \text{ \AA}$	$\mu = 0.078 \text{ mm}^{-1}$
$b = 10.9620 (1) \text{ \AA}$	$T = 298 (2) \text{ K}$
$c = 13.2238 (1) \text{ \AA}$	Rectangular
$\alpha = 67.053 (1)^\circ$	$0.40 \times 0.35 \times 0.20 \text{ mm}$
$\beta = 84.532 (1)^\circ$	Light yellow
$\gamma = 68.754 (1)^\circ$	
$V = 1143.98 (2) \text{ \AA}^3$	
$Z = 2$	
$D_x = 1.282 \text{ Mg m}^{-3}$	
$D_m$ not measured	

#### Data collection

Siemens CCD diffractometer	$R_{\text{int}} = 0.039$
$\omega$ scans	$\theta_{\text{max}} = 26.99^\circ$
Absorption correction: none	$h = -12 \rightarrow 12$
13 224 measured reflections	$k = -15 \rightarrow 15$
4909 independent reflections	$l = -18 \rightarrow 18$
3396 reflections with $I > 2\sigma(I)$	

#### Refinement

Refinement on $F^2$	$\Delta\rho_{\text{max}} = 0.202 \text{ e \AA}^{-3}$
$R[F^2 > 2\sigma(F^2)] = 0.045$	$\Delta\rho_{\text{min}} = -0.213 \text{ e \AA}^{-3}$
$wR(F^2) = 0.130$	Extinction correction: <i>SHELXTL-Plus</i> (Sheldrick, 1995)
$S = 1.015$	Extinction coefficient: 0.028 (3)
4907 reflections	Scattering factors from <i>International Tables for Crystallography</i> (Vol. C)
308 parameters	
H atoms not refined	
$w = 1/[\sigma^2(F_o^2) + (0.07P)^2]$	
where $P = (F_o^2 + 2F_c^2)/3$	
$(\Delta/\sigma)_{\text{max}} < 0.001$	

### Compound (6b)

#### Crystal data

C <sub>42</sub> H <sub>32</sub> N <sub>4</sub> O <sub>2</sub>	Mo K $\alpha$ radiation
$M_r = 624.72$	$\lambda = 0.71073 \text{ \AA}$
Monoclinic	Cell parameters from 8192 reflections
$P2_1/n$	$\theta = 2.0\text{--}20.0^\circ$
$a = 11.1257 (1) \text{ \AA}$	$\mu = 0.080 \text{ mm}^{-1}$
$b = 15.4692 (2) \text{ \AA}$	$T = 223 (2) \text{ K}$
$c = 18.7765 (1) \text{ \AA}$	Rectangular
$\beta = 91.135 (1)^\circ$	$0.44 \times 0.34 \times 0.20 \text{ mm}$
$V = 3230.91 (5) \text{ \AA}^3$	Yellow
$Z = 4$	
$D_x = 1.284 \text{ Mg m}^{-3}$	
$D_m$ not measured	

#### Data collection

Siemens CCD diffractometer	$R_{\text{int}} = 0.035$
$\omega$ scans	$\theta_{\text{max}} = 28^\circ$
Absorption correction: none	$h = -15 \rightarrow 15$
30 368 measured reflections	$k = -21 \rightarrow 21$
7796 independent reflections	$l = -25 \rightarrow 26$
6251 reflections with $I > 2\sigma(I)$	

*Refinement*Refinement on  $F^2$  $R[F^2 > 2\sigma(F^2)] = 0.043$  $wR(F^2) = 0.106$  $S = 1.019$ 

7782 reflections

441 parameters

H-atom treatment mixed (see below)

$$w = 1/[\sigma^2(F_o^2) + (0.0451P)^2 + 1.0P]$$

where  $P = (F_o^2 + 2F_c^2)/3$ 

$$(\Delta/\sigma)_{\max} = 0.001$$

$$\Delta\rho_{\max} = 0.248 \text{ e } \text{Å}^{-3}$$

$$\Delta\rho_{\min} = -0.230 \text{ e } \text{Å}^{-3}$$

Extinction correction: none

Scattering factors from

*International Tables for Crystallography* (Vol. C)

Preliminary examination and data collection were performed using a Siemens CCD automated single-crystal X-ray diffractometer, using graphite-monochromated Mo  $K\alpha$  radiation. Intensity data were collected using  $\omega$  scans and a double-pass method was used to avoid spurious peaks. The first 50 frames of data were recollected at the end of the data collection to monitor crystal decay. No absorption corrections were applied to the data. Non-H atoms were refined anisotropically to convergence. Only the H atoms connected to C5 and C6 in the case of (6b) were refined freely. Other H atoms were treated as riding [ $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$  and  $\text{C}-\text{H} = 0.95 \text{ \AA}$ ].

For all compounds, data collection: *SMART* (Siemens, 1995); cell refinement: *SAINT* (Siemens, 1995); data reduction: *SAINT*; program(s) used to solve structures: *SHELXTL-Plus* (Sheldrick, 1995); program(s) used to refine structures: *SHELXTL-Plus*; molecular graphics: *SHELXTL-Plus*; software used to prepare material for publication: *SHELXTL-Plus*.

We thank the Council of Scientific and Industrial Research, Government of India (DR and MVG), the Jawaharlal Nehru Center for Advanced Scientific Research, Bangalore, India (MVG), NSF (CHE-9101834), Missouri Research Board, Center for Molecular Electronics and the Department of Chemistry of the University of Missouri–St Louis (NPR), and the Office of the Basic Energy Sciences of the US Department of Energy [MVG (in part)], for financial support of this work. This is document No. NDRL-4012 from the Radiation Laboratory and No. RRLT-PRU-87 from the Regional Research Laboratory, Trivandrum, India.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1078). Services for accessing these data are described at the back of the journal.

**References**

- Angadiyavar, C. S., Sukumaran, K. B. & George, M. V. (1971). *Tetrahedron Lett.* pp. 633–636.
- Bauer, H., Bedford, G. R. & Katritzky, A. R. (1964). *J. Chem. Soc.* pp. 751–752.
- Curtin, D. Y. & Alexandrou, N. E. (1963). *Tetrahedron*, **19**, 1697–1703.
- Grammaticakis, P. (1947). *C. R. Acad. Sci.* **224**, 1509–1511.
- Jones, R., Liu, Z., Scheffer, J. R. & Trotter, J. (1995). *Acta Cryst.* **B51**, 888–892.
- Pechman, H. von (1897). *Chem. Ber.* **30**, 2461–2463.
- Ramaiah, D., Rath, N. P. & George, M. V. (1997). Unpublished results; coordinates available from N. P. Rath.

Sheldrick, G. M. (1995). *SHELXTL-Plus. Program for the Solution and Refinement of Crystal Structures*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Siemens (1995). *SAINT and SMART*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Stolle, R. (1926). *Chem. Ber.* **59**, 1742–1747.

Sukumaran, K. B., Angadiyavar, C. S. & George, M. V. (1972). *Tetrahedron*. pp. 3987–3998.

*Acta Cryst.* (1998). **C54**, 875–877

**2-[(Z)-2-(p-Anisidino)-3,3,3-trifluoropropenyl]-4,4-dimethyl-2-oxazoline**

MALVA LIU-GONZALEZ,<sup>a</sup> FRANCISCO SANZ-RUÍZ,<sup>a</sup> ANTONIO NAVARRO-MARTINEZ,<sup>b</sup> MARTA GARCÍA DE LA TORRE<sup>b</sup> AND SANTOS FUSTERO-LARDIES<sup>b</sup>

<sup>a</sup>Departamento de Termología, Facultad de Física, Universidad de Valencia, Dr. Moliner, 50, 46100 Burjassot (Valencia), Spain, and <sup>b</sup>Departamento de Química Orgánica, Facultad de Farmacia, Universidad de Valencia, Avda. Vte. Andrés Estelles s/n, 46100 Burjassot (Valencia), Spain. E-mail: liu@evalryr.scsi.uv.es

(Received 28 January 1997; accepted 18 November 1997)

**Abstract**

The title compound,  $\text{C}_{15}\text{H}_{17}\text{F}_3\text{N}_2\text{O}_2$ , is a C-protected N-substituted  $\beta$ -enamino acid derivative. Bond lengths suggest  $\pi$  conjugation between the oxazoline (4,5-dihydro-1,3-oxazole) ring and the enamine double-bond moiety. Intramolecular hydrogen bonding is found between the N atom attached to the aromatic ring and the heterocyclic N atom. Because of steric hindrance between the aromatic ring and the trifluoromethyl group, the plane of the former adopts an almost perpendicular position with respect to the oxazoline ring plane.

**Comment**

Acyclic  $\beta$ -enamino acid derivatives (Bartoli *et al.*, 1995) have been used frequently as intermediates in the synthesis of natural products and other synthetic compounds possessing biological activity. They are regarded as important building blocks in the synthesis of alkaloids (Cook *et al.*, 1994),  $\beta$ -amino acids and  $\beta$ -lactams (Bartoli *et al.*, 1994), among others, and they have also been applied with success in asymmetric syntheses (Potin *et al.*, 1990; Ando *et al.*, 1994). Furthermore, if such compounds contain F atoms, they are even more attractive for use in the fields of medicinal