BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 45, 515—519 (1972)

The Photochemical Decomposition of Benzotriazoles

Kazuo Tsujimoto, Mamoru Ohashi, and Teijiro Yonezawa
Department of Hydrocarbon Chemistry, Faculty of Engineering Kyoto University, Kyoto

(Received March 24, 1971)

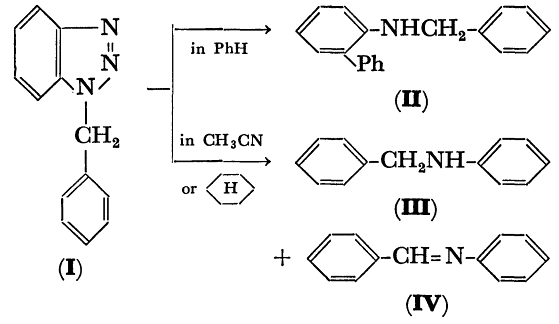
The photochemical decomposition of several 1-substituted benzotriazoles was investigated. It was observed that in contrast to the thermolytic decompositions of 1-benzyl and 1-benzoylbenzotriazole, the intermediates produced by the loss of nitrogen from these compounds upon irradiation react with hydrogen-donating solvents to yield either reduced or substituted products. The possibility of the presence of an antiaromatic benzoazacyclopropene as an intermediate can be excluded on the basis of the fact that the photolysis of 4′,5-dichloro-1-phenylbenzotriazole gave 3,6-dichlorocarbazole as the sole product. The acetone-sensitized photolysis of 1-benzoylbenzotriazole causes a Wolff rearrangement giving a cyclopentadiene derivative. On the basis of extended Hückel molecular orbital calculations on the intermediates, it is concluded that the photochemical loss of nitrogen from benzotriazoles gives excited-state 1,3-diradicals, while the thermolytic decompositions afford ground-state ones.

Recently Burgess and his co-workers[1] found that the photolysis of 1-phenylbenzotriazole gave carbazole quantitatively. In a previous paper,[2] we reported that the photolysis of various benzotriazoles gave products different from those of thermal decompositions. This fact implies that the spin-correlation effects[3] may be observed in these decomposition process, just as in the case of azides.[4]

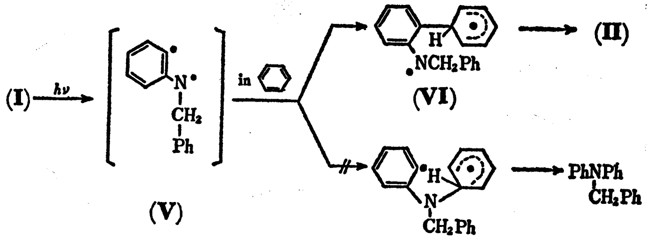
To shed some light on the nature of the intermediates produced upon the irradiation of some benzotriazoles, we have examined the difference of benzotriazoles; we based our examination on a molecular-orbital consideration of the electronic structure of the diradical intermediates.

Results and Discussion

The photolysis of 1-benzylbenzotriazole (**I**) in benzene gave *N*-(2-biphenylyl)benzylamine (**II**) in a 29% yield; this amine was the only product which was isolated by column chromatography on silica gel. However, when **I** was photolyzed in acetonitrile, **IV** was obtained together with benzylaniline (**III**), which must be produced by hydrogen abstraction from the solvent (**III** : **IV**=1 : 5).



In the photochemical reaction of **I**, two manners must be considered for the addition of benzene to the diradical (**V**), as shown in Scheme 1.



Scheme 1

It is more reasonable to assume that the more reactive center in the diradical (**V**), which presumably has the character of a reactive σ-radical, adds to benzene,[5] and that intramolecular hydrogen transfer in the

---

[1] E. M. Burgess, R. Carithers, and L. McCullagh, *J. Amer. Chem. Soc.*, **90**, 1923 (1968).

[2] M. Ohashi, K. Tsujimoto, and T. Yonezawa, *Chem. Commun.*, **1970**, 1089.

[3] P. D. Bartlett and P. S. Engel, *J. Amer. Chem. Soc.*, **90**, 2960 (1968).

[4] J. S. Swenton, T. J. Ikeler, and B. H. Williams, *ibid.*, **92**, 3103 (1970).

[5] D. H. Hey, *Adv. Free Radical Chem.*, **2**, 47 (1967).

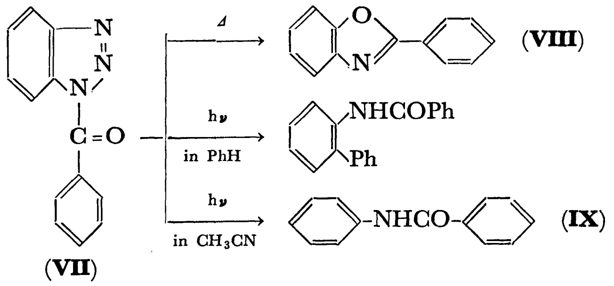
resulting adduct (**VI**) then leads to the observed product. When the photolysis of **I** was carried out in cyclohexane, which is thought to be more hydrogen-donating to the produced diradical than is acetonitrile,⁶⁾ benzylaniline (**III**) was obtained together with benzylideneaniline (**IV**) (**III**:**IV**$=6:1$).

The formation of **IV** in cyclohexane implies that the diradical resulting from the benzotriazole can abstract intramolecularly a hydrogen atom, even in a hydrogen-donating solvent.

Gibson has reported,⁷⁾ that the thermolysis of **I** gave phenanthridine, a cyclized product, in a small yield. However, in the photolysis of **I** we could obtain neither phenanthridine nor 9,10-dihydrophenanthridine, not even in acetonitrile (checked by glpc).

This difference in behavior between the thermolysis and photolysis of **I** suggests that the ground-state diradical of **V** is liable to cyclize and that the diradical produced upon irradiation is either an excited singlet or triplet state and that it abstracts a hydrogen atom intramolecularly or from a solvent cage.

The same sort of difference in behavior between the thermolysis and photolysis is also observed in the case of 1-benzoylbenzotriazole. Drulliner reported⁸⁾ that 1-benzoylbenzotriazole (**VII**) decomposed in diphenyl ether at a reflux temperature to give 2-phenylbenzoxazole of **VIII** in an 11% yield. However, in our experiments, only a trace of **VIII** could be obtained in its photolysis in acetonitrile (probably less than 1%). The major product was the amide (**IX**) which had been produced *via* a 1,3- or 1,5-diradical intermediate through hydrogen abstraction from the solvent. The fact that **VIII** could not be obtained in the photolysis of **VII** is analogous to the case of the photolysis of 1-benzylbenzotriazole (**I**), where neither phenanthridine nor 9,10-dihydrophenanthridine was obtained.



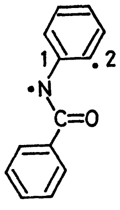
The difference in behavior between the thermolytic and photolytic decomposition of **VII** can be interpreted by means of an extended Hückel MO investigation of the electronic structure of the intermediate (**XI**). The atomic-bond populations of C$_2$-O cited in Table 1 (see Experimental section) show that it is bonding in the ground state but antibonding in the excited state. These results are consistent with the experimental results; that is the thermolytic⁸⁾ or mass spectrometric⁹⁾ decomposition of **VII** gives the cyclized product, while the photolytic one gives **VIII** in only a small amount.

Table 1. Total energy and atomic bond populations of **XI**.

	Ground state	Excited state
Total Energy	−1313.6 eV	−1311.8 eV
Atomic Bond Population of C$_2$-N	−0.180	−0.178
Atomic Bond Population of C$_2$-O	0.050	−0.006

These arguments point to the facts that the thermolytic decomposition of **VII** gives the ground state of **XI** and that the photolysis produces the excited state.

When the photolysis of **VII** was acetone-sensitized, benzanilide (**IX**) and a new type of compound (**X**) were obtained. The assignment of the structure of **X** rests on analytical and spectroscopic data as follows. The results of elemental analysis and the molecular peak (*m*/*e* 253) of the mass spectrum indicate that its molecular formula is $C_{16}H_{15}NO_2$, suggesting the addition of a molecule of acetone to the diradical intermediate (**XI**). The presence of a strong conjugated carbonyl absorption at 1650 cm^{-1} in the IR spectrum and a strong benzoyl peak at *m*/*e* 105 in the mass spectrum suggest the benzoyl group. Further information about the structure is obtained from the 220 MHz NMR spectrum. A singlet peak at δ 1.93 (6H) indicates two methyl groups. The complex ABCX signals were demonstrated in the region between δ 5.5 and δ 7.0 in Chart 1; the spectrum given at the bottom was obtained by computer simulation with LAOCOON III.¹⁰⁾



(**XI**)

From these spectral data, two structures, (**X**) and (**X′**), are conceivable. Considering the chemical

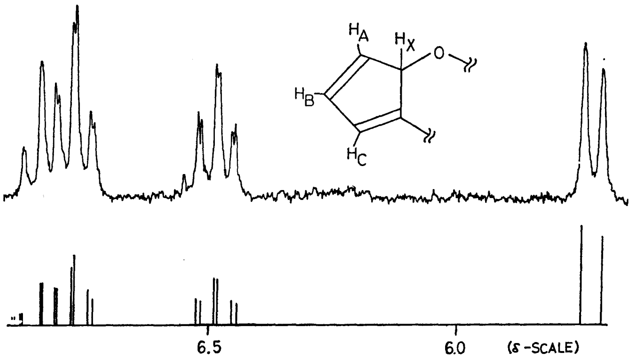


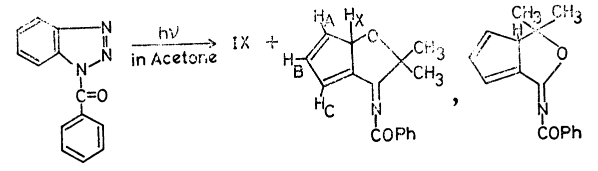
Chart 1. A part of 220 MHz NMR spectrum of **X**.

---

6) P. Flowerday and M. J. Perkins, *J. Chem. Soc.*, **1970**, 298.
7) M. S. Gibson, *ibid.*, **1956**, 1076.
8) J. D. Drulliner, *J. Amer. Chem. Soc.*, **90**, 6879 (1968).
9) M. Ohashi, K. Tsujimota, A. Yoshino, and T. Yonezawa, *Org. Mass Spectrometry*, **4**, 203 (1971).

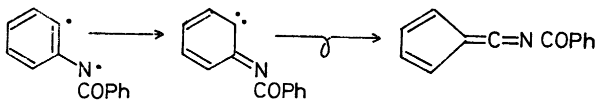
10) The resulting parameters were $J_{XA}=J_{AB}=J_{BC}=7.5$ Hz, $J_{AC}=1.5$ Hz, and $J_{XB}=0.6$ Hz; the others were zero. A. A. Bother-By and S. M. Castellano, *J. Chem. Phys.*, **43**, 3863 (1964).

shift of the H_x proton (δ, 5.73 ppm), we concluded that the structure (**X**) must be favored over **X**'.



(**VII**) (**X**) (**X**')

The formation of **X** implies that the reaction proceeds *via* the intermediate (**XI**) formed by triplet acetone-sensitization, which is presumably transformed into the more stable iminofulvene (**XII**') through an iminocarbene (**XII**), followed by Wolff rearrangement. No product corresponding to **X** was obtained in the acetophenone- and benzophenone-sensitized photolyses.



(**XI**) (**XII**) (**XII**')

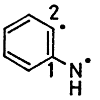
These results suggest that the reactions of these intermediates are intimately related to their electronic structures. Therefore, it becomes important to clarify the electronic structure of the intermediates. Boyer and Selvanjan investigated the photolysis of several benzotriazoles and concluded that the 1,3-diradical intermediates have carbene-like structures.[11]

We carried out MO calculations on **XIII**', which has a fundamental, simple skelton, by means of the extended Hückel method.

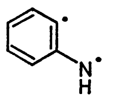
Table 2. Atomic and atomic bond polulations of **XIII**'.

	N	C_2
N	6.618	−0.186
C_2	−0.186	3.689

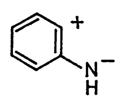
Extended Hückel calculation indicates that the atomic-bond population between C_2 and N is negative (antibonding), and that the atomic-bond populations[12] on the N and C_2 atoms have negative and positive charges respectively. These calculations suggest that the possibility of making a bond between N and C_2 to produce benzoazacyclopropene (**XIIIc**') is quite small and that the dipolar character predominant over the diradical structure (**XIIIa**').



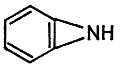
(**XIII**')



(**XIIIa**')



(**XIIIb**')

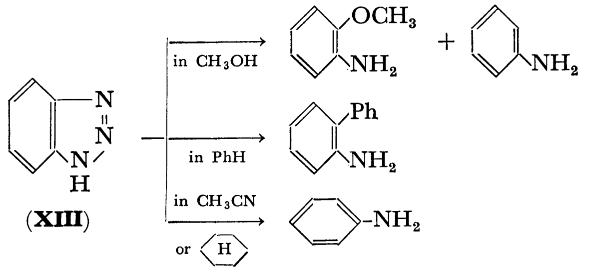


(**XIIIc**')

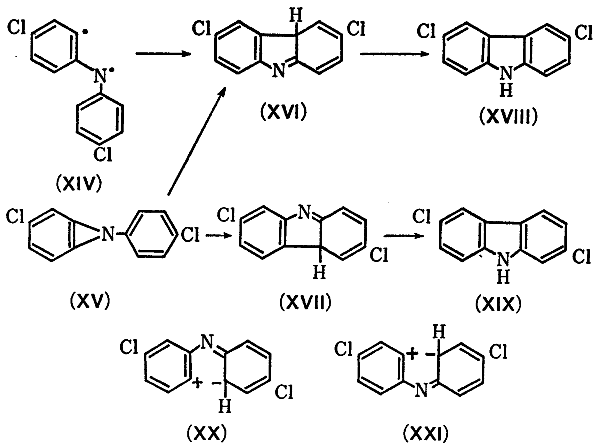
The same calculations also show that the benzoazacyclopropene (**XIIIc**') is less stable than the associated dipolar intermediate, the difference in their total energies being 3.4 eV (=78 kcal).

In accordance with these calculations, the photolysis of 1H-benzotriazole (**XIII**) in methanol gave *o*-anisidine as a major product (70% yield), along with aniline (30% yield). On the other hand, the photolysis of **XIII** in benzene gave *o*-biphenylamine in a 32% yield, and the similar irradiation of **XIII** in acetonitrile and in cyclohexane gave aniline in 6% and 20% yields respectively.

These results suggest that the character of the intermediate (**XIIIa**' or **XIIIb**') depends on the polarity of the solvent.



Although these molecular orbital calculations indicate that the intermediate (**XIII**') has no tendency to form benzoazacyclopropene (**XIIIc**'), an antiaromatic compound,[13] we attempted to prove this prediction experimentally. Thus, we examined the behavior of 4',5-dichloro-1-phenylbenzotriazole upon irradiation. The structures of the resulting carbazole were identified by means of the NMR spectra. 3,6-Dichlorocarbazole was isolated as the sole aromatic product in an 89% yield. No 2,6-dichlorocarbazole (**XIX**) was detected, even in the NMR specta of the unpurified product mixture.



If the intermediate was not **XIV** but **XV**, a comparable amount of **XVII** with **XVI** would be obtained in the case of the homolytic cleavage of the azirine ring in **XV**, while the antisymmetric carbazole (**XIX**)

---

[11] J. H. Boyer and R. Selvanjan, *J. Heterocycl. Chem.*, **6**, 503 (1969).

[12] R. Hoffman, *J. Chem. Phys.*, **39**, 1397 (1963); R. S. Mulliken, *ibid.*, **23**, 1833, 1841, 2338, 2343 (1955).

[13] R. Breslow, J. Brown, and J. J. Gajewski, *J. Amer. Chem. Soc.*, **89**, 4383 (1967).

would be produced when the heterolytic cleavage took place, because the positive charge of **XX** should be more stabilized than that of **XXI** in terms of the electronegativity of the chlorine atom at the *para* position.[14]

In conclusion, we have examined the photochemical decompositions of several 1-substituted benzotriazoles and have found that the photochemical decompositions of 1-benzyl and 1-benzoylbenzotriazoles give products different in their thermolytic and mass spectrometric decompositions.[9] This difference in behavior is accounted for in terms of the electronic structures of the diradical intermediates.

The photochemical loss of nitrogen from the benzotriazoles gives the excited-state intermediates, while the thermolytic decomposition must afford the electronic ground-state intermediates. One exception is the case of 1-phenylbenzotriazole, where both thermolytic and photolytic decompositions[1] gives carbazole almost quantitatively.

In this case, we have no evidence to confirm whether or not the same electronic structute of the intermediates must be considered in both reactions. A detailed investigation of the electronic multiplicities of the intermediates based on SCF-ASMO-CI calculations are now in progress.

Experimental

The IR spectra were recorded on a Hitachi Model 215 grating spectrometer.

The NMR spectra were recorded for solutions in deuteriochloroform (unless otherwise stated) with a Varian HR-220 apparatus, using TMS as the internal standard. The mass spectra were obtained on a double-focussing mass spectrometer, Model JMS-01SG. All the mps were measured on a micro hot stage and are not corrected.

Photolysis of ***I***. *(A) In Benzene*: The triazole (1.0 g) was dissolved in benzene (500 m*l*), which had previously dried over phosphorus pentoxide and purified by distillation; the solution was than irradiated for 4 hr under a nitrogen atmosphere with a 200-W high-pressure mercury arc lamp surrounded by a quartz filter. The solvent and low-boiling-point materials were removed under reduced pressure. The reaction mixture thus obtained indicated two spots on tlc (silica gel) and was chromatographed on silica gel. Elution with methylene dichloride gave the unreacted triazole and **II** (40 mg); mp 87—88°C (lit, 84—86°C), mass spectrum M$^+$, 259 (93), 180 (32), 167 (28), 91 (100), IR-(KBr), ν_{NH} 3500 cm^{-1}.

(B) In Acetonitrile: The triazole (1.39 g) was irradiated in acetonitrile (330 m*l*) for 13 hr with a 200-W high-pressure mercury lamp. After the removal of the solvent under reduced pressure, the residue was chromatographed on basic alumina. Elution with benzene gave an orange-yellow oil (120 mg), which was discovered by means of vpc analysis using a column of 5% PEG 20 M on chromosorb G to be a mixture of two products. These products had the same retention times as had benzylaniline and benzylideneaniline respectively. The product ratio was determined by vpc using diphenylamine as the internal standard. The oil was rechromatographed on basic alumina, and subsequent elution with cyclohexane - benzene (3 : 1) gave **III** and **IV**, whose structures were identified by the comparison of their IR spectra with the standard IRDC cards.

Photolysis of 1-Benzoylbenzotriazole. (A) In Benzene: A solution of the triazole (1.0 g) in benzene (500 m*l*) was irradiated with a 200-W high-pressure mercury arc lamp for 4 hr under a nitrogen atmosphere. The solvent was then removed *in vacuo*, and the residue was chromatographed on silica gel (200 mesh 30ϕ × 190 mm). Elution with methylene chloride (200 m*l*) recovered the unreacted triazole (600 mg). Further elution (400 m*l*) gave a solid (60 mg), which was then crystallized from ligroin to give *N*-(2-biphenylyl)benzamide (mp 88°C). Its IR spectrum was identical with that of an authentic sample. Elution with ethyl acetate and methanol gave polymeric materials which were not identified.

(B) In Acetonitrile: The triazole (120 mg) in acetonitrile (20 m*l*) was irradiated with a 5-W low-pressure mercury lamp for 2 hr under a nitrogen atmosphere. The solvent was then removed *in vacuo*. The residue was chromatographed on silica gel (200 mesh 10 g) with methylene chloride, thus giving three cuts. From the first fraction we obtained 21 mg of the unreacted triazole. The second one gave 9 mg of colorless needles which had a mp of 160—161°C; its IR spectrum agreed with that of the IRDC card of benzaniline. The third fraction gave an identified polymeric material.

(C) In Acetone: A solution of the triazole (1.02 g) in acetone (240 m*l*) was irradiated with a 10-W low-pressure mercury lamp for 15.5 hr under a nitrogen atmosphere. The solvent was then removed. The residue was chromatographed on silica gel. Subsequent elution with methylene dichloride gave three products, whose R_f values on tlc were 0.90, 0.70, and 0.40. The R_f 0.90 fraction (310 mg) turned out to be the unreacted triazole, while the R_f 0.40 fraction (93 mg) was identified as benzanilide by a comparison of its IR spectrum with that of the authentic sample. The recrystallization of the R_f 0.70 fraction (78 mg) from ethanol-water gave colorless needles which melted at 122.0—122.5°C; *m/e* 253 (M$^+$), λ_{max} 311 nm (EtOH), ν_{max} (KBr) 1650 cm^{-1}, δ1.93(s. 6H), 5.73 (d.d. 1H J=7.5 Hz and 0.6 Hz), 6.84(t.d. 1H, J=7.5 and 1.5 Hz), 6.75(d.d. 1H, J=7.5 and 1.5 Hz), 6.84 (t.d. 1H J=7.5 Hz, and 0.6 Hz), and 7.5(m. 5 H) ppm.

Found: C, 75.59; H, 5.86; N, 5.53%. Calcd for $C_{16}H_{15}NO_2$: C, 75.59; H, 5.97; N, 5.53%.

(D) In Acetophenone: The triazole (1.0 g) was dissolved in freshly-distilled acetophenone (240 m*l*). The solution was then irradiated with a low-pressure mercury lamp (10 W) for 13 hr under a nitrogen atmosphere. The solvent was then removed *in vacuo* (max. bath temp. at 63°C). The tlc of the residue on silica gel indicated that almost all of the material was the unreacted triazole. The residue was chromatographed on silica gel. Subsequent elution with benzene gave the starting material and polymeric materials whose structures were not identified.

(E) In Benzophenone: The triazole (500 mg) and benzophenone (508 mg) were dissolved in chloroform (80 m*l*). The solution was irradiated with a high-pressure mercury arc lamp (100 W), using a 2-mm pyrex filter, for 10 hr under a nitrogen atmosphere. The reaction mixture was chromatographed after the removal of the solvent in order to establish the recovery of the starting material.

*Photolysis of 1*H*-Benzotriazole. (A) In Methanol*: The triazole (1.0 g) in methanol (500 m*l*) was irradiated with a 200-W high-pressure mercury arc lamp for 18.5 hr. The solvent was then removed *in vacuo*, and the residue was chromatographed on silica gel. Elution with methylene

---

[14] M. S. Ao. E. M. Burgess, A. Schauer, and E. A. Taylor, *Chem. Commun.* **1969**, 220,

dichloride gave a red-brown oil (136 mg). A part of the oil was distilled *in vacuo* to give *o*-anisidine, whose IR spectrum was identical with that of an authentic sample. The vpc of the oil on a column of 15% PEG 20 M on Chromosorb W showed the same retention time as that of *o*-anisidine. However, the vpc analysis of the total product showed the presence of an additional product which had the same retention time as that of aniline. A careful vacuum distillation of the oily product gave a colorless oil whose structure was identified by a comparison of its IR spectrum with the IRDC card of aniline.

(B) In Benzene. A benzene solution (500 m*l*) of 1*H*-benzotriazole (1.0 g) was irradiated with a high-pressure mercury arc lamp under bubbling nitrogen gas for 6 hr. The solvent was removed *in vacuo*, and then the residue was chromatographed on silica gel to give biphenylamine (164 mg), whose structure was identified by a comparison of its IR spectrum with the standard IRDC card.

Photolysis of 4′,5-dichloro-1-phenylbenzotriazole. The triazole (104 mg) was irradiated in acetonitrile (20 m*l*) for 14 hr. The solvent was then removed, and the residue was chromatographed on silica gel. Subsequent elution with benzene gave colorless needles (81 mg); mp 200.5—201.2°C (lit: 202°C)[15]: IR spectrum (KBr) ν_{NH} 3530 cm^{-1}; *m/e* 237(64), 253(100), and 200(64).

The NMR spectrum showed resonances at δ7.03 (2H, A part of ABX pattern), 7.21 (2H, B part), 7.83 (2H, X part), and 10.0 (br. s. 1H) ppm acetone.

The calculation by means of the extended Hückel method has been described in detail by Hoffmann.[12] The resonance integrals were evaluated by the following equation:

$$KS_{rs}(H_{rr}+H_{ss})/2,\ K=1.75.$$

The Coulomb integrals were estimated by the use of $H_{rr}=-I_p$, where I_p is the ionization potential of the appropriate valence state.

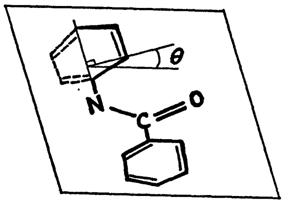
The following values were used in the text:

H	−13.6 eV	
C	−21.43	−11.42
N	−27.5	−14.47
O	−35.3	−15.45

The total energy calculated on the basis of various conformations of **XI** is summarized in Table 3.

Table 3. Dihedral angles θ and total energy

θ	Total Energy (eV)
0	−1313.580
10	−1313.576
90	−1313.559
180	−1312.361



The numerical calculations were carried out at the Kyoto University Computation Center. (FACOM 230—60)

The authors wish to express their hearty thanks to Professor Hiroshi Kato of Nagoya University for his kind advice.