New Models for the Study of the Racemization Mechanism of Carbodiimides. Synthesis and Structure (X-ray Crystallography and ^{1}H NMR) of Cyclic Carbodiimides

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The crystal and molecular structure of carbodiimides **2** (5,6,18,19-tetradehydro-5,12,13,18,25,26-hexahydrotetrabenzo[*d*,*h*,*m*,*q*][1,3,10,12]tetraazacyclooctadecine) and **3** (8,10,22,24-tetraazapentacyclo-[23.3.1.1^{3,7}.1^{11,15}.1^{17,21}]dotriaconta-1(29),3,5,7(32),8,9,11,13,15(31),17,19,21(30),22,23,25,27-hexadecaene) have been determined. The activation barriers for the racemization of carbodiimides **1** (6,7-dihydrodibenzo[*d*,*h*][1,3]diazonine), **2**, and **3** have been determined. While **1** presents a relatively high barrier (17.4 kcal mol^{-1}), **2** and **3** have very low activation barriers (between 5 and 7 kcal mol^{-1}). We tentatively conclude that open-chain and large-ring carbodiimides racemize by nitrogen inversion or *trans*-rotation while medium-size cyclic carbodiimides racemize by *cis*-rotation.

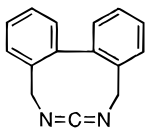
Cyclic carbodiimides have been the subject of theoretical and spectroscopic studies in an attempt to examine the configurational stability of nitrogen in the N=C=N linkage.[1−4] The problem is related to the "inversion" *vs* "rotation" mechanisms in imines, especially *N*-phenylimines (Schiff bases).[5] The following summary of what is known of the isomerization mechanism of carbodiimides is based on the work of Hiatt,[1] Gordon,[6] Anet,[7] Damrauer,[2] and Firl (ketenimine **III**):[8] Most results, as those obtained for structures **I**−**III,** concern nine-membered rings closely related to our compound **1**.

(i) Open-chain carbodiimides have an energy barrier of racemization of 6.7 ± 0.2 kcal mol^{-1}.[7]

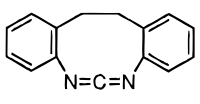
(ii) There are three possible mechanisms for the isomerization:[6] inversion, *cis*-rotation, and *trans*-rotation. According to MP4/6-311G** calculations for the parent carbodiimide (HN=C=NH), the corresponding barriers are 10.6, 8.0, and 7.9 kcal mol^{-1} respectively.

(iii) A nine-membered ring cyclic carbodiimide (1,3-diazacyclonona-1,2-diene, **II**) has the same barrier, 6.7 ± 0.2 kcal mol^{-1}.[2] The ring appears to add nothing to the barrier, so in light of the above discussion, this suggest that with five flexible CH_2−CH_2 bonds, the ring places no constraint on the change of configuration of the carbodiimide.

(iv) A contrast is presented by another nine-membered ring carbodiimide, the compound **I**. From the description of its ^{1}H-NMR spectrum given by Hiatt (diastereotopic chemical shifts not reported, only J_{gem} = 15.4 Hz),[1] the interconversion is slow at room temperature, and reasonable assumptions linked to this observation suggest the barrier is at least 15.0 kcal mol^{-1}. It is already well-known that in such bridged biphenyls the barrier is dominated by the biphenyl bond rotation, although the bridge may contribute somewhat to the barrier.[9]



I



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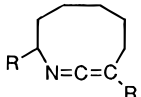
II



III

In spite of the implications of this last example, Damrauer[2] has suggested that cyclic compounds might give an indication of the relative importance of nitrogen

[⊗] Abstract published in *Advance ACS Abstracts,* June 1, 1996.

(1) Hiatt, R. R.; Shaio, M.-J.; Georges, F. *J. Org. Chem.* **1979**, *44*, 3265.
(2) Damrauer, R.; Soucy, D.; Winkler, P.; Eby, S. *J. Org. Chem.* **1980**, *45*, 1315.
(3) Richter, R.; Tucker, B.; Ulrich, M. *J. Org. Chem.* **1983**, *48*, 1694.
(4) Johnson, R. P. *Chem. Rev.* **1989**, *89*, 1111.
(5) Jennings, W. B.; Wilson, V. E. Trigonal Nitrogen in *Acyclic Organonitrogen Stereodynamics*, Lambert, J. B.; Takeuchi, Y., Eds.; VCH Press: New York, NY, 1992; Chapter 6.
(6) Nguyen, M. T.; Riggs, N. V.; Radom, L.; Winnerwisser, M.; Winnerwisser, B. P.; Birk, M. *Chem. Phys.* **1988**, *122*, 305.
(7) Anet, F. A. L.; Jochims, J. C.; Bradley, C. H. *J. Am. Chem. Soc.* **1970**, *92*, 2557.
(8) Firl, J.; Schink, K.; Kosbahn, W. *Chem. Lett.* **1981**, 527.
(9) Sutherland, I. O.; Ramsay, M. J. V. *Tetrahedron* **1965**, *21*, 3401.

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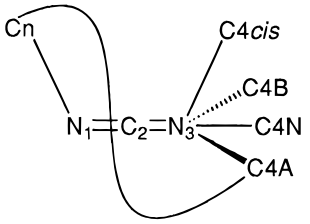
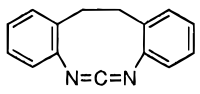
inversion and rotation about a C=N bond for isomerization of carbodiimides. This interaction is attractive, as the diagram below shows for an *n*-membered ring. Locating atoms Cn, N1, C2, and N3 in the plane of the paper, one configuration has C4 in front of the plane as shown by C4A. The interconversion process takes C4 to position C4B either by nitrogen inversion via position C4N, or by rotation about a C=N bond through a transition state C4*cis* where C4 and Cn are *cis* in the same plane. The ground-state distance Cn−C4A or Cn−C4B is greater than Cn−C4*cis* but less than Cn−C4N. The chain of the ring, which has to bridge positions C4 and Cn should have an optimum conformation which will hopefully have a marked preference for one of these interconversion pathways, one of which stretches the chain and the other shortens it. In particular, the link between Cn and C4 excludes the *trans*-rotation mechanism for medium-size cyclic carbodiimides.

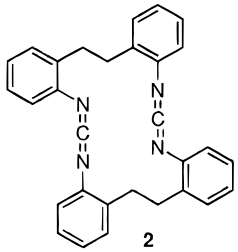


(v) For ketenimines the barrier for the open-chain compound is 14.1 kcal mol^{-1}, while for compound **III** (R = benzyl) 19.3 kcal mol^{-1}, $\delta\Delta G^{\ddagger} = 5.2$ kcal mol^{-1}.[8] Firl considered both the inversion ($\delta\Delta G^{\ddagger} > 0$) and the *cis*-rotation ($\delta\Delta G^{\ddagger} < 0$) mechanisms, concluding that nitrogen inversion mechanism is preferred in ketenimines.

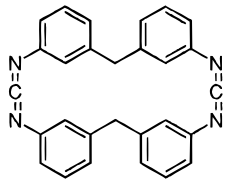
Recently we reported the preparation of a series of cyclic carbodiimides from bis(iminophosphoranes),[10,11] among them compounds **1**−**3**.



1



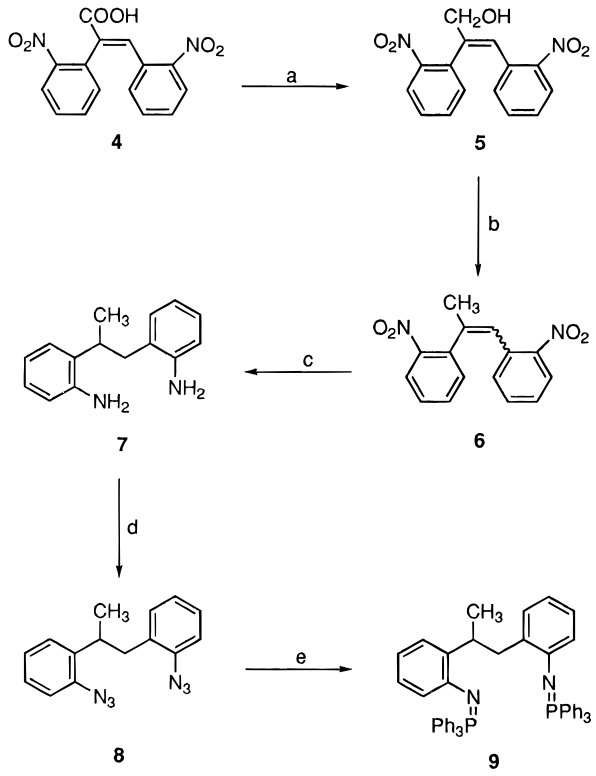
2



3

6,7-Dihydrodibenzo[*d*,*h*][1,3]diazonine **1** is a nine-membered ring cyclic carbodiimide, for which molecular mechanics and semiempirical calculations (AM1) led to the same conformation for the fully optimized geometry.[11] This system is quite rigid and there should be a high barrier to any interconversion (nitrogen and/or ring inversion). Keeping this is mind, the presence of a chiral center in the ethane bridge would give rise to diastereoisomeric cyclic carbodiimides capable of being separated. Such a compound would be of interest in the study of the mechanism of racemization of this heterocumulene functionality.

Scheme 1



4 **5** **6** **7** **8** **9**

Reagents: a) $NaBH_4$ / $TiCl_4$ (55 %); b) i, CH_3SO_2Cl, Et_3N, ii, $NaBH_4$, HMPA / H_2O (73 % overall yield); c) H_2, Pd / C (89 %); d) i, $NaNO_2$, HCl,ii, NaN_3 (95 %); e) Ph_3P (82 %).

On the other hand, cyclic bis(carbodiimides) such as **2** and **3** may be too large (18- and 20-membered rings) to observe fluxionality by NMR. Thus the objectives of the present work are as follows: (i) to prepare and determine, by ^{1}H NMR, the conformation of nine-membered cyclic carbodiimides (derivatives of **1**) bearing substituents at the ethane bridge; and (ii) to study, by dynamic ^{1}H NMR, the fluxionality of cyclic carbodiimides **1**−**3** and to determine their X-ray crystal structures.

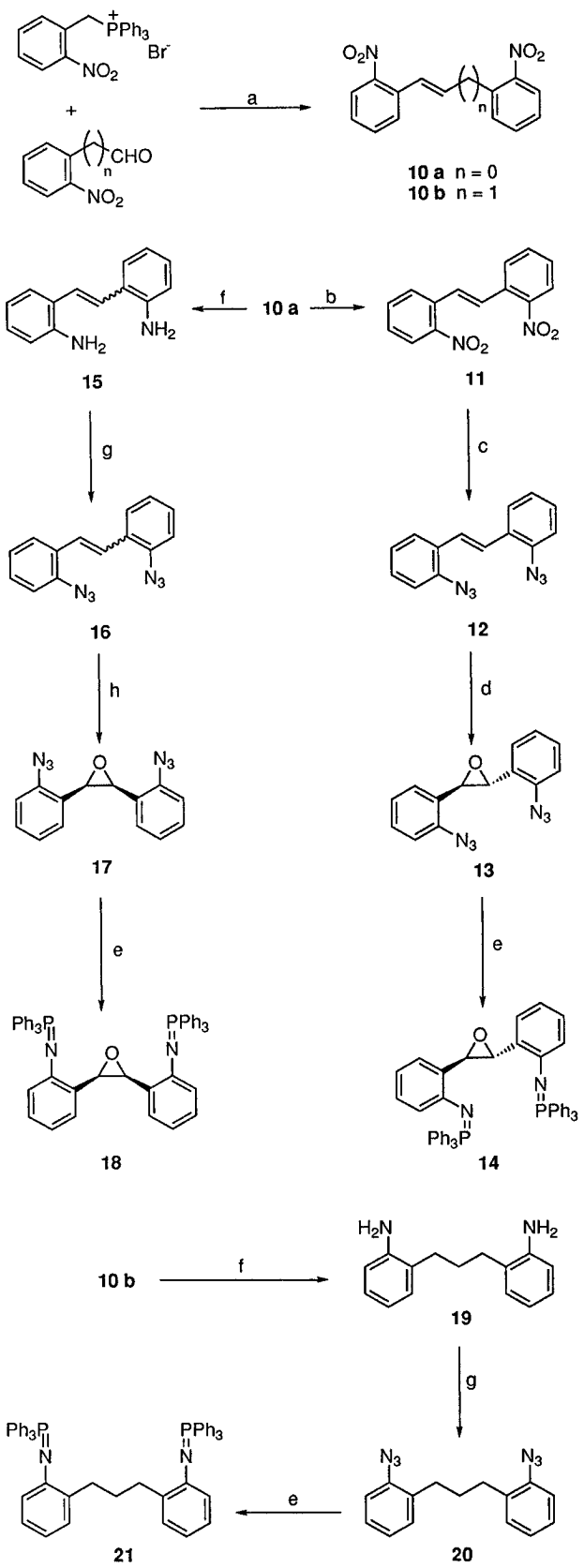
Results and Discussion

Chemistry. The previously unreported bis(iminophosphoranes) **9**, **14**, and **18** were prepared by Staudinger reaction of the corresponding bis(azides) with triphenylphosphane. The bis(azide) **8** was prepared from stilbene derivative **4**, available by condensation of the *o*-nitrophenylacetic acid with *o*-nitrobenzaldehyde in 78% yield, by conversion of the carboxylic group into a methyl group, reduction of both nitro− and carbon−carbon double-bond functionalities and finally diazotization/azidation (Scheme 1). The isomeric bis(azides) **13** and **17** were prepared from **10a** by the sequence: reduction of the nitro groups, diazotization/azidation, and further epoxidation . Bis(iminophosphorane) **21** was also prepared by a similar sequence, starting from **10b** (Scheme 2).

Conversion of bis(iminophosphoranes) into cyclic carbodiimides was achieved by three methods: (i) reaction with 2 equiv of Boc_2O in the presence of 1 equiv of DMAP

(10) Molina, P.; Alajarín, M.; Sánchez-Andrada, P. *Tetrahedron Lett.* **1993**, *34*, 5155.
(11) Molina, P.; Alajarín, M.; Sánchez-Andrada, P.; Elguero, J.; Jimeno, M. L. *J. Org. Chem.* **1994**, *59*, 7306.

Scheme 2



Reagents: a) K_2CO_3 / CH_2Cl_2 / dibenzo-18-crown-6 (65-95 %); b) PhSH, AIBN, Δ (80 %); c) i, Fe, AcOH, EtOH , ii, $NaNO_2$, HCl, then NaN_3 (86 % overall yield); d) *m*-CPBA (72 %); e) Ph_3P (80-95 %); f) Fe, AcOH, EtOH (90 %); g) $NaNO_2$, HCl then NaN_3 (80-93 %); h) *m*-CPBA then separation of the isomers by column chromatography (42 %).

in dichloromethane at room temperature (method A); (ii) reaction with carbon dioxide in dry benzene at 70 °C in a sealed tube (method B); and (iii) reaction with an excess of carbon disulfide (20 equiv) in benzene at reflux temperature and further addition of 1 equiv of starting bis(iminophosphorane) (method C).

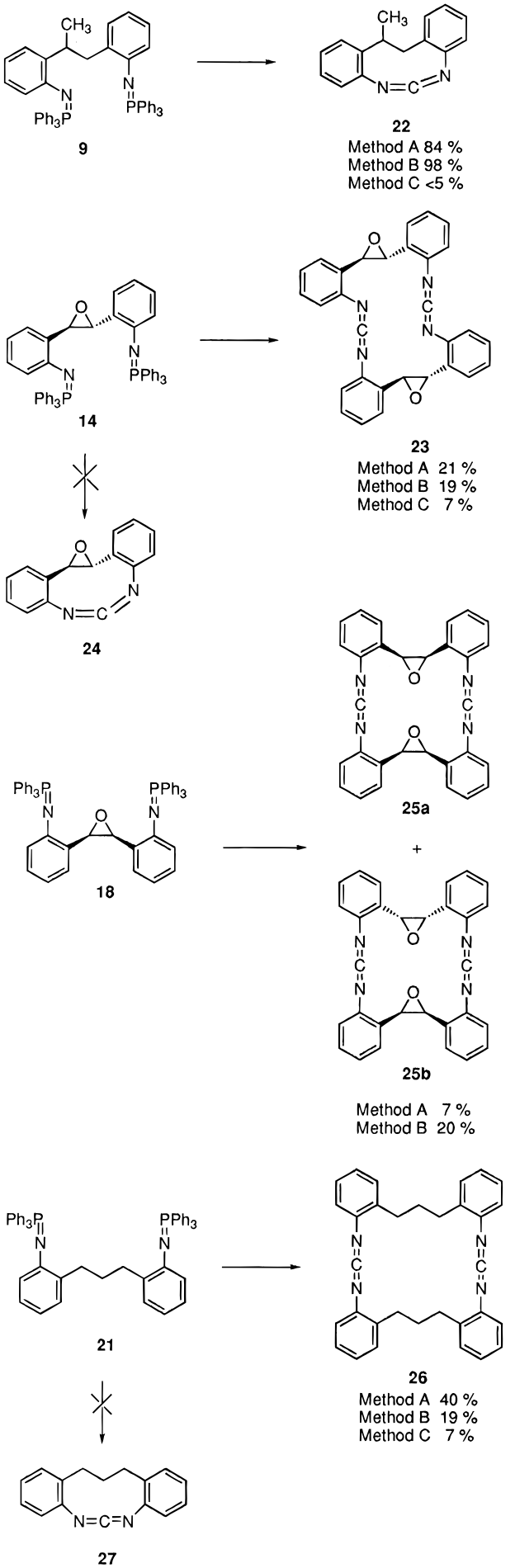
Bis(iminophosphorane) **9** was converted into the nine-membered cyclic carbodiimide **22**, and the method of choice was found to be method B. However, the bis-(iminophosphorane) **14** led to the cyclic carbodiimide **23** as the only reaction product in modest yields, method A being that which afforded the higher yield (21%). It is not easy to explain why the cyclic carbodiimide **24** was not formed in this reaction, because molecular modeling of this compound reveals that the torsion angle between the two hydrogen atoms in the oxirane ring is similar to the one observed in the closely related carbodiimide **1**. The bis(iminophosphorane) **18** provided a 1:1 mixture of two isomeric cyclic bis(carbodiimides) **25a** and **25b**, from which only one was isolated in pure state by fractional crystallization. Finally, the cyclic bis(carbodiimide) **26** was obtained as a crystalline solid in modest yields from the bis(iminophosphorane) **21**, and no traces of the expected cyclic carbodiimide **27** could be detected in the crude product (Scheme 3).

X-ray Crystallography. Cyclic carbodiimides described in this and the previous paper[11] were used to obtain suitable crystals. After many attempts, only those of compounds **2** (5,6,18,19-tetradehydro-5,12,13,18,25,26-hexahydrotetrabenzo[*d*,*h*,*m*,*q*][1,3,10,12]tetraazacyclooctadecine) and **3** (8,10,22,24-tetraazapentacyclo-[23.3.1.$1^{3,7}$.$1^{11,15}$.$1^{17,21}$]dotriaconta-1(29),3,5,7(32),8,9,11,13,15(31),17,19,21(30),22,23,25,27-hexadecaene) were of good quality.

The final X-ray models of compounds **2** and **3**, drawn with ORTEP (see also ref 28),[12] are shown in Figures 1 and 2. In both cases, the molecules are arranged about crystallographic inversion centers. The unit cell of **3** contains two crystallographically independent molecules, thus the crystallographic asymmetric part is formed by two independent half-molecules, which show only slight differences in the torsional angles. In the carbodiimide moiety, the averaged N−C bond length is 1.21 Å (compound **2** and molecules 1 and 2 of compound **3**). The valence angles at the carbodiimide C atoms are respectively 166.8(3)° for compound **2** and 167.8(4) and 168.7(4)° for molecules 1 and 2 of compound **3**. The torsional angles around N×01-C×14 are 134(2)° for both molecules of compound **3**, not far away from the mean value of 134° (range 112−142°) obtained from other carbodiimides (MXPCIM, NIPCIM, PMCBIM, TOCDIM, VOJPEP)[13] while the corresponding torsional angle around N1−C14 in compound **2** is 156(1)°, showing greater angular deformation. The geometry of the N=C=N part compares well with the calculated geometry of HN=C=NH: *d*(N=C) = 1.21−1.23 Å, NCN angle = 168−170°.[14] No voids are found in these crystal structures, the total packing coefficient being 0.69 for both compounds.[15] We have summarized in Table 1 some geometrical characteristics of compounds **2** and **3** and the five retrieved structures from the CSD. We will use the same descrip-

(12) Johnson, C. K. ORTEP, Report ORNL-3974, Oak Ridge National Laboratory, TN, 1965.
(13) Allen, F. H.; Davies, J. E.; Galloy, J. J.; Johnson, O.; Kennard, O.; Macrae, C. F.; Mitchell, E. M.; Smith, J. M.; Watson, D. G.; *J. Chem. Info. Comput. Sci.* **1991**, *31*, 187.
(14) Bertrán, J.; Oliva, A.; Jose, J.; Duran, M.; Molina, P.; Alajarín, M.; López-Leonardo, C.; Elguero, J. *J. Chem. Soc., Perkin Trans. 2* **1992**, 299.
(15) Cano, F. H.; Martínez-Ripoll, M. *J. Mol. Struct.* (*THEOCHEM*) **1992**, *258*, 139.

Scheme 3



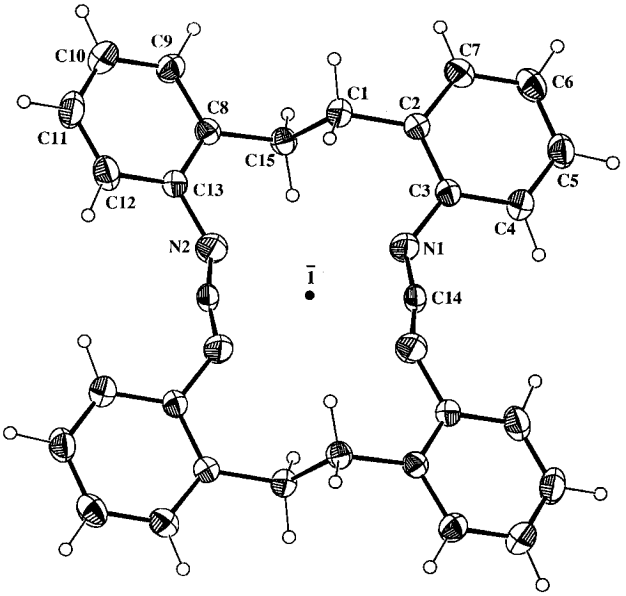


Figure 1. Compound **2** showing the atomic numbering used.

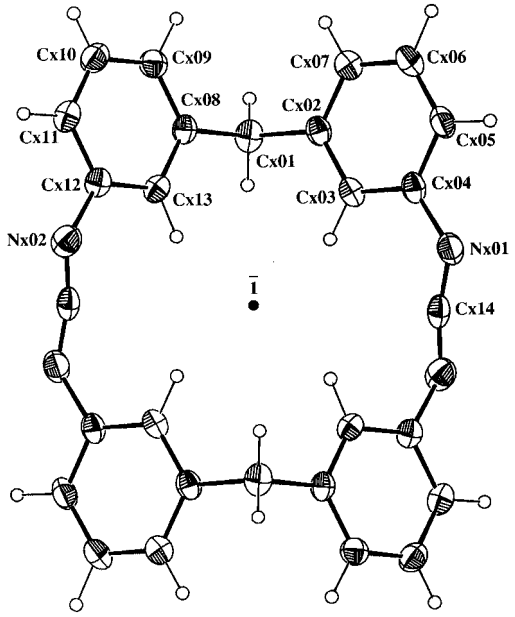


Figure 2. Compound **3** showing the atomic numbering used ($x = 1, 2$ for molecules 1 and 2).

Table 1. X-ray Geometries of Carbodiimides

	angle, deg			
compd	dihedral θ	C=N−Ph_1	C=N−Ph_2	N=C=N
2	98	135	136	166.8
3	57	130	131	168.2
MXPCIM	95	129	130	169.0
NIPCIM	114	130	134	170.0
PMCBIM	95	125	126	170.0
TOCDIM	88	127	128	170.0
VOJPEP	92	128	130	168.0

tors for the semiempirical calculations (see below). The angles C=N−Ph and N=C=N are similar but the small "dihedral" angle θ (Ph−N···N−Ph) in compound **3** (57°) shows that its ring strain is larger than that of compound **2** ($\theta = 98°$).

^{1}H NMR Spectroscopy. Compound **22** shows only a methyl signal and a complex system of protons at 300 MHz, but all signals are narrow. Since compound **22** can exist in two conformations **22a** and **22b** (Scheme 4), this implies either a rigid conformation (**22a** or **22b**) or a rapid

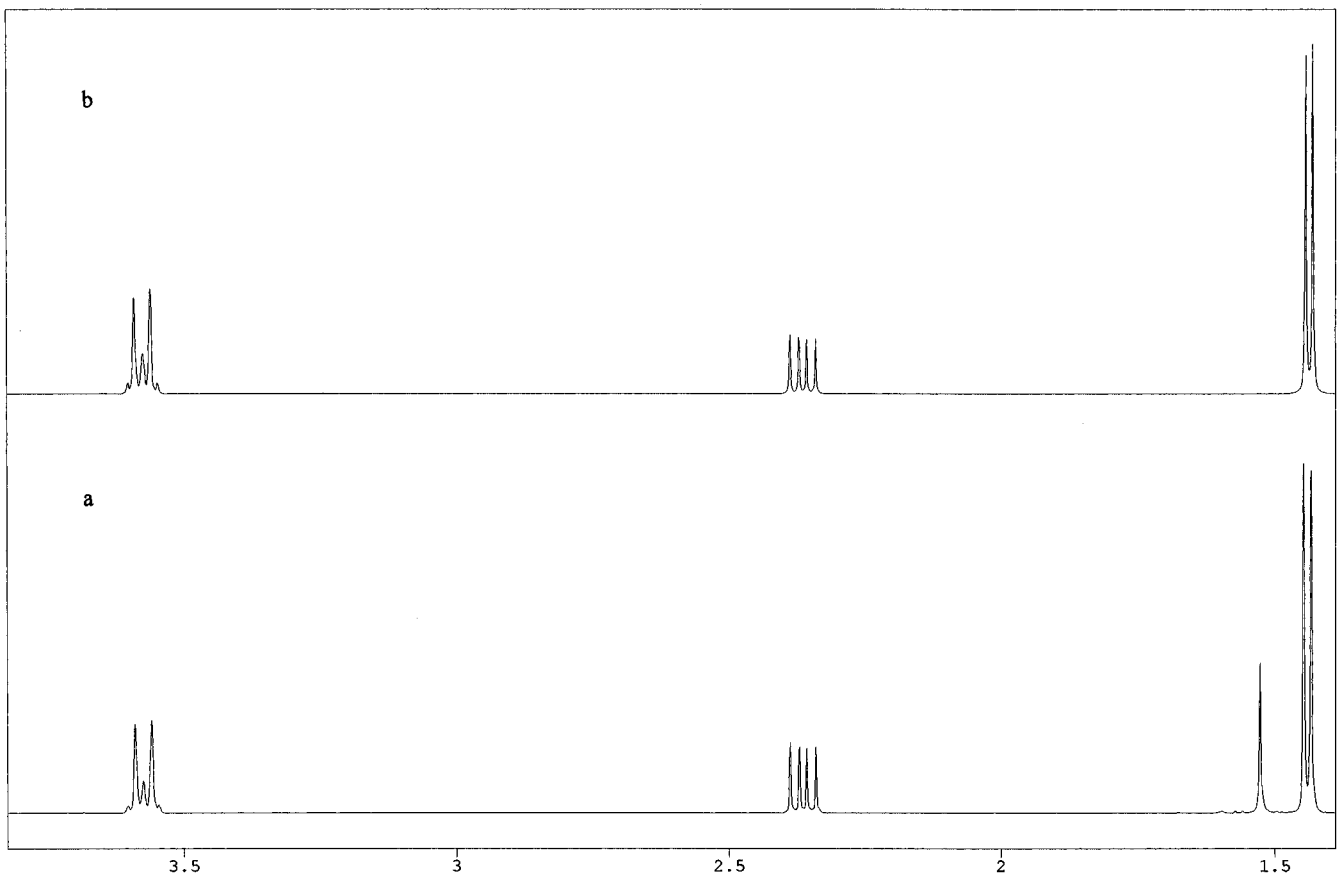
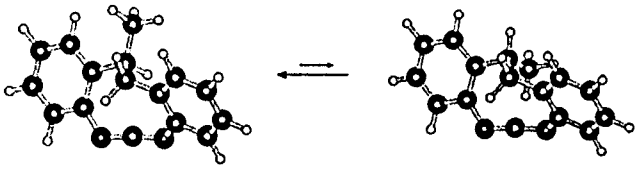


Figure 3. Experimental (a) and calculated (b) ^{1}H NMR spectra of compound **22**.

Scheme 4



22a **22b**

Table 2. ^{1}H-NMR Data (δ, ppm; J, Hz) of Dibenzodiazonines 1 and 22

atom	δ	fragment	$J(^1H-^1H)$
	Compound **1** (acetone, 298 K)		
H1 (H4)	3.129	H1,H2 (H3,H4)	−15.56
H2 (H3)	3.200	H1,H3 (H2,H4)	7.58
		H1,H4	11.97
		H2,H3	1.52
	Compound **22** ($CDCl_3$, 298 K)		
Me1	1.445	Me1,H2	6.43
H2	3.582	Me1,H3	0
H3	3.583	Me1,H4	0
H4	2.372	H2,H3	1.05
		H2,H4	8.33
		H3,H4	−15.27

ring plus nitrogen inversion. In our previous paper[11] we stated that compound **1** exists at room temperature in a rigid conformation; we have now the possibility to confirm or reject this conclusion.

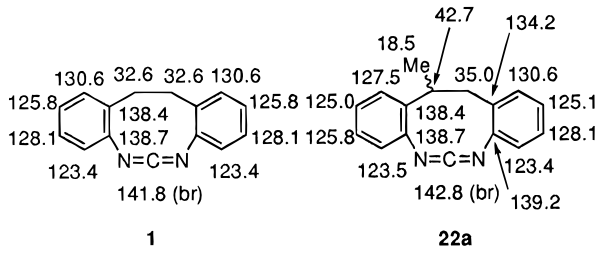
Figure 3 shows the experimental and calculated ^{1}H-NMR spectrum of compound **22**, and Table 2 reports the data for the ethane fragment of compounds **1**[11] and **22**. Small couplings between these protons and aromatic protons[11] have been neglected in the case of compound **22**. Structure **22a**, methyl "out", results formally from replacing H1 in compound **1** by Me while structure **22b**, methyl "in", results from replacing H2 by Me. Thus, in the case of **22a** a J(H2,H3) ≈1.5 Hz is expected while for **22b** a J(H1,H4) ≈12 Hz is expected.

Since the replacement of the proton by a methyl group slightly modifies the conformation of **1** as well as the constant term in the Karplus equation, it is possible that the values estimated for **22** are slightly erroneous. An alternative approach is to minimize the geometry of both isomers (using the AM1 Hamiltonian like in the case of **1**)[11] and to calculate the ^3J(H,H) coupling constants using the Karplus relationship. The compound with the methyl "out" **22a** is calculated to be more stable than its isomer **22b** by 4.4 kcal mol^{-1}, the dihedral angles [and the corresponding vicinal coupling constants between square brackets] are as follows: **22a** H2,H4 = 144.32° [8.45 Hz]; H2,H3 = −101.22° [1.50 Hz]; **22b** H1,H4 = 11.17° [10.07 Hz]; H1,H3 = 123.58° [4.91 Hz].

The experimental values (Table 1) are 8.33 and 1.05 Hz, so there is no doubt that the structure of the methyl derivative is **22a**. Since in the case of compound **1** no modification of the spectrum was observed until 183 K, the previous conclusion of a rigid system is the only possibility.[11] The calculation of the spectrum was a little complicated due to the accidental coincidence of the chemical shifts of H2 and H3 (Table 1). We have observed in another context (Δ^2-pyrazolines) that the replacement of a proton by a methyl group in an ethane fragment results in a deceptively simple ^{1}H-NMR spectrum due to accidental coincidence of the *geminal* proton and the proton *gauche* to the methyl group (the proton *cis* to the methyl group is shifted upfield by the anisotropy of the methyl single bonds).[16]

(16) Elguero, J.; Fruchier, A. *J. Chem. Res.* **1990** (S) 200; (M) 1501.

The ^{13}C NMR spectrum of compound **1** shows a signal at 32.6 ppm ($CDCl_3$); in compound **22a** there are three signals in the saturated part of the spectrum ($CDCl_3$): 18.5 (Me), 35.0 (CH_2) and 42.7 (CH). No signals corresponding to **22b** were observed. The assignment of these spectra is represented below:



Since in open-chain carbodiimides, the central N=C=N carbon atom appears at ~132 ppm,[17] the shift to ~142 ppm in compounds **1** and **22a** probably reflects change of hybridization due to angular strain.

Dynamic ^1H NMR Spectroscopy. Since the methylene proton signal of **1** appears as an AA′BB′ system at room temperature, interconversion of enantiomeric conformations must be slow on the NMR time scale. On raising the temperature of a [$^2H_8$]toluene solution of **1**, lines began to broaden, and eventually coalesce at 369 K. Making the simplifying assumption that this can be treated as the coalescence of an AB-quartet ($J_{AB} = -15.56$ Hz,[11] $\nu_A = 747.33$ Hz and $\nu_B = 907.20$, $\nu_0\delta = 159.87$ Hz), the values for the racemization of carbodiimide **1**, $k_c = 365.1\ s^{-1}$ and $\Delta G_c^{\ddagger} = 17.4$ kcal mol^{-1} both at 369 K, were obtained. Compound **1** is dramatically more rigid than open-chain carbodiimides, but this barrier to interconversion is too low to allow resolution of chiral structures.

The spectrum of compound **22** contrast in behavior with that of **1** as it consists of a single set of signals (the minor isomer has to be present in a very minor amount since a 100 multiplication of the intensity does not show another methyl doublet) which does not change significantly over the temperatures range −90 °C to +80 °C. By analogy with **1**, conformational processes should be slow on the NMR time scale in **22**, so following the discussion given above, the observation of a single set of signals indicates that one conformation, presumably **22a** with methyl "out" (and its enantiomer) is much more stable than the other **22b** with methyl "in".

Compounds **2** and **3** have much more flexible structures. Compound **3** was studied at 400 MHz using vinyl bromide/CD_2Cl_2 4:1 approximately as solvent. The CH_2 signal broadens in comparison with a reference peak from about 166 K downward and is very broad at 136 K, but the solution froze at 134 K, twice. The coalescence temperature is expected to be 131 K at the lowest. Assuming a reasonable chemical shift, the rate constant might be as much as 400 s^{-1} at 131 K and the lower limit for the barrier ($k = 400\ s^{-1}$ at 131 K) should be 5.9 kcal mol^{-1}. A reasonable estimate for the barrier is 6.2 ± 0.3 kcal mol^{-1}. Compound **2** was studied at 400 MHz in a mixture of $CHF_2Cl/CHFCl_2/CD_2Cl_2$, ca. 3:1:1. At 147 K the CH_2 proton signal is broad (10 Hz) compared with the solvent (3 Hz); at 133 K crystallization of the solute appeared to have taken place and no spectrum was seen. On the basis of reasonable assumptions for the relative shift of prochiral protons the ring inversion barrier is at most 7 kcal mol^{-1}, but in view of the greater broadening observed for **3**, probably less than this, indeed somewhat less than the 6.2 kcal mol^{-1} which was estimated for **3**.

The experimental observation is of geminal protons changing from being diastereotopic on the NMR time scale at "low" temperature to being enantiotopic at "high" temperature, so we think these molecules processes are taking place which interconvert chiral structures. A simple equation allows us to calculate a barrier to this process for each molecule, but the temperatures at which changes take place and thus the barriers are markedly higher for **1** than for **2** and **3**, and we want to discuss what may be involved in these processes.

In acyclic dialkyl-substituted carbodiimides it is reasonable to assume that the energy necessary to change the configuration of the carbodiimide determines the barrier, the two alkyl groups rearranging their conformation as may be necessary at some late stage, without affecting the barrier size. With cyclic derivatives, this may once again be the case, but there is another possibility, that the rearrangement of the ring conformation may be constrained, and so may contribute to or even dominate the barrier that is measured.

It is plausible that if the chain joining the two ends of the carbodiimide is flexible, as is the case when the chain has many bonds about which rotation takes place easily, the change in configuration at the carbodiimide determines the measured barrier size, and the barriers are then small, around 6−8 kcal mol^{-1}. If the chain has few bonds about which rotation takes place easily (or has one bond with a high barrier about which rotation must take place), then the conformation requirements of the ring overall may determine the measured barrier size.

Replacement of a CH_2—CH_2 bond in a medium-size ring with an inflexible CH=CH bond reduces the conformational mobility of the ring, and if that double bond is incorporated as a benzene ring the effect is even greater. Many examples of this can be extracted from tabulations of ring-inversion barriers in medium-size rings such as that given by Anet and Anet.[18] It is thus reasonable to suggest that in **1** and **I**, the observed barrier owes less to carbodiimide isomerization (although this has to take place to render protons equivalent on the NMR time scale) than to their dibenzannelated ring structure.

Probably, open-chain carbodiimides and large-size rings like **2** and **3** would racemize by the inversion or *trans*-rotation mechanisms with barriers between 6 and 8 kcal mol^{-1} while medium-size cyclic carbodiimides, **1** and **I**, would racemize by the *cis*-rotation mechanism. To have a numerical estimation of ring-size effects on the racemization of diarylcarbodiimides we have carried out a series of AM1 calculations in which compound **1** is compared with diphenylcarbodiimide **IV** (Table 3). Although we have already used succesfully the AM1 Hamiltonian for describing carbodiimides,[11,14] we have checked the validity of these calculations in the case of carbodiimide itself **V**. As we have reported in the introduction, this molecule has been subjected to very high level calculations.[6] The results gathered in Table 3 confirm the validity of the AM1 Hamiltonian both in terms of energy and geometry. Note that the geometry of **IV** (ground state) is close to the average geometry of

(17) Heinisch, G.; Matuszczak, B.; Pürstinger, G.; Rakowitz, D. *J. Heterocycl. Chem.* **1995**, *32*, 13.

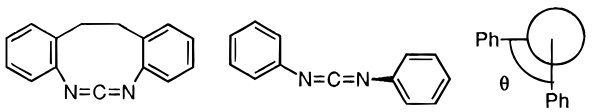
(18) Anet, F. A. L.; Anet, R. Conformational Processes in Rings. In *Dynamic Nuclear Magnetic Resonance Spectroscopy*; Jackman, L. M., Cotton, F. A., Eds.; Academic Press: New York, 1985; Chapter 14.

Table 3. AM1 calculations (Enthalpy Values in kcal mol^{-1})[a]

compound		ground state	(inversion)‡	(*cis*-rotation)‡	(*trans*-rotation)‡
1	dihedral angle θ, deg	74.2	19.3	**0**	**180**
	C=N−Ph_1 angle, deg	121.2	**180**	125.5	----
	C=N−Ph_2 angle, deg	121.2	113.6	125.5	----
	N=C=N angle, deg	173.8	161.2	163.4	----
	$\delta\Delta H$	0[b]	27.8	8.4	----
IV	dihedral angle θ, deg	102.2	172.9	**0**	**180**
	C=N−Ph_1 angle, deg	125.8	**180**	135.4	136.0
	C=N−Ph_2 angle, deg	125.8	122.5	135.4	136.0
	N=C=N angle, deg	166.6	171.3	154.9	180.0
	$\delta\Delta H$	0[c]	10.5	10.0	7.1
1-IV	$\delta\delta\Delta H$	0	17.3	−1.6	----
V	dihedral angle θ, deg	100.0	2.6	**0**	**180**
	C=N−H_1 angle, deg	120.1	**180**	131.1	131.4
	C=N−H_2 angle, deg	120.1	118.4	131.1	131.4
	N=C=N angle, deg	167.4	169.6	156.3	180.0
	$\delta\Delta H$	0[d]	11.5	10.6	7.6
V[e]	dihedral angle θ, deg	89.6	**0**	**0**	**180**
	C=N−H_1 angle, deg	119.7	172.0	131.2	130.9
	C=N−H_2 angle, deg	119.7	118.6	131.2	130.9
	N=C=N angle, deg	170.8	173.4	168.5	180.0
	$\delta\Delta H$	0	10.6	8.0	7.9

[a]Angles imposed (constrains) are in bold. [b] ΔH = 105.53 kcal mol^{-1}. [c] ΔH = 106.64 kcal mol^{-1}. [d] ΔH = 41.41 kcal mol^{-1}. [e] MP4/6-311G**.[6]

the five open-chain diarylcarbodiimides found in the CSD (Table 1: 97°, 129°, 129°, 169°).



1 **IV**

In the case of compound **1**, the *trans*-rotation is a meaningless process since the N=C=N and CH_2−CH_2 groups must crossover. Of the remaining two processes, the *cis*-rotation mechanism is preferred although the calculated barrier (8.4 kcal mol $^{-1}$) is lower than the experimental one (17.4 kcal mol^{-1}). For the open-chain compound **IV**, the values are in excellent agreement with the calculations (both AM1 and MP4) for carbodiimide itself **V**, showing that the hydrogen atoms can be replaced by phenyl groups without significant changes in the relative energies. Assuming that some errors will cancel when comparing the energies involved in compounds **1** and **IV** ($\delta\delta\Delta H$), it appears that a relatively short chain joining the two ends of the diphenylcarbodiimide facilitates the *cis*-rotation (by about 2 kcal mol^{-1}), increases considerably the energy of the inversion process (by about 17 kcal mol^{-1}), and renders impossible the *trans*-rotation mechanism.

Concluding Remarks

Assuming that the activation barrier determined for **1** (17.4 kcal mol^{-1}) is similar for **22** it can be concluded that if there were a mixture of **22a** and **22b** present in solution, two methyl signals and two ABC(X_3) systems should have been observed at room temperature in ^{1}H-NMR, but the clear preference for methyl "out" **22a** over methyl "in" **22b** prevent this observation. Probably, two groups of similar size on the same sp^3 carbon would be necessary to observe both isomers (for instance, CH_3 and CD_3). Moreover, the barrier is too low for enantiomers to be separated (separation requires $\Delta G^{\ddagger}$ > 30 kcal mol^{-1}), so there is little hope in obtaining a chiral carbodiimide whose chirality lies on the carbodiimide group. To this aim ring strain is not an automatic solution, since in some forms it makes racemization more difficult but in others makes it easier.

Although quite different in shape (**2** is an 18-membered ring and **3** is a 20-membered ring) these large systems have similar flexibility.

Experimental Section

General Methods. ^{1}H and ^{13}C NMR spectra were recorded on a Varian Unity 300 apparatus (Murcia) (^{1}H at 299.95 MHz and ^{13}C at 74.43 MHz), and chemical shifts are expressed in parts per million (δ) relative to tetramethylsilane (error in temperature measurements ±0.1 °C). The ^{1}H NMR spectra of compound **22** were recorded at 30 °C on a Varian Unity-500 spectrometer (Madrid) operating at 499.84 MHz, using $CDCl_3$ as solvent. The spectra were acquired using 3967.1 Hz spectral width, digitized with 32K data points with a pulse width of 7 μs (90° flip angle). Digital resolution for the real part was ±0.25 Hz. Gaussian multiplication was used prior to Fourier transform. The ^{1}H-NMR iterative analysis of the spectrum was performed using the PANIC program.[19] Variable-temperature experiments on compounds **2** and **3** were carried out on a Varian VXR 400 spectrometer (London) operating at 400 MHz.

Crystal Structure of Compounds 2 and 3. A summary of the crystallographic data is given in Table 4. The structures were solved using SIR92.[20] Slight secondary extinction effects[21] were corrected during the last cycles of least-squares refinement.

Computational Calculations. The AM1 Hamiltonian[26] was used within its original formalism. In all cases, the

(19) PANIC 86, Bruker Program Library, Germany.
(20) Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, G.; Giacovazzo, G.; Guagliardi, A.; Polidori, G. SIR92. *J. Appl. Crystallogr.* **1995**, in preparation.
(21) Larson, A. C. *Acta Crystallogr.* **1967**, *23*, 664.
(22) Stewart, J. M.; Machin, P. A.; Dickinson, C. W.; Ammon, H. L.; Heck, H.; Flack, H. *The X-Ray 80 System*; Computer Science Center, Univ. of Maryland: College Park, MD, 1985.
(23) Martínez-Ripoll, M.; Cano, F. H. PESOS. *Computer program for the automatic evaluation of l.s. weights;* Instituto 'Rocasolano', CSIC; Madrid, Spain, 1975.
(24) Nardelli, M. *Comput. Chem.* **1983**, *7*, 95.
(25) *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, 1974; Vol. IV, p 72.
(26) Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1977**, *99*, 4899; 4907 (AMPAC V2.1, QCPE program No. 506).

Table 4. Experimental Data and Structure Refinement Procedures

crystal data	(**2**)	(**3**)
formula	$C_{30}H_{24}N_4$	$C_{28}H_{20}N_4$
crystal habit	colorless prisms	colorless prisms
crystal size (mm)	0.17 × 0.23 × 0.60	0.18 × 0.27 × 0.30
symmetry	monoclinic $P2_1/n$	monoclinic $P2_1/a$
unit cell determination	LS fit from 63 refl (θ < 30°)	LS fit from 54 refl (θ < 28°)
unit cell dimen. (a,b,c), Å	14.587(2), 5.4087(4),15.082(2)	9.601(1), 10.642(1), 21.272(1)
(β), deg	107.00(1)	95.08(1)
packing: V (Å^3), Z	1137.9(2), 2	2164.9(3), 4
D_c (g cm^{-3}), M, F(000)	1.29, 440.5, 464	1.27, 412.49, 864
(cm^{-1})	5.9	5.9
experimental data		
technique:	four circle diffractometer, SEIFERT XRD-3000S bisecting geometry graphite-oriented monochromator: CuKα (λ = 1.5418 Å) $\omega/2\theta$ scans, scan width (deg): 1.5 + 0.15 tan θ detector apertures 2 × 2°	
	θ_{max} = 60°	θ_{max} = 65°
no. of reflections:		
measured	1761	3845
independent	1691	3515
observed	968 [2$\sigma(I)$ criterion]	1923 [2$\sigma(I)$ criterion]
range of hkl	−16 16, 0 6, 0 16	−11 11, 0 13, 0 25
max sin θ/λ	0.562	0.590
value of R_{int}	0.004	0.004
standard reflections	2 reflections every 100 reflections; no variation	
solution and refinement		
solution	direct methods	
refinement	least squares on F_{obs}, full matrix	
parameters:		
no. of variables	191	350
degrees of freedom	777	573
ratio of freedom	5.1	5.5
H atoms	difference synthesis	difference synthesis
maximun final shift/error	0.003 (U_{13} of C15)	0.004 (x of H213)
w-scheme	empirical as to give no trends in $\langle w\Delta^2F\rangle$ vs $\langle F_o\rangle$ or $\langle \sin\theta/\lambda\rangle$	
max thermal value	0.082 (U_{22} of C11)	0.088 (U_{22} of N201)
final ΔF peak	0.22 e/Å^3	0.12 e/Å^3
extinction coefficient[21]	0.0019(1)	0.004(1)
S, unit weight standard deviation	1.16	0.83
final R and R_w	0.041, 0.046	0.036, 0.035
computer and programs	VAX6410, SIR92,[20] XRAY76,[22] PESOS,[23] PARST[24]	
scattering factors	*Int. Tables for X-Ray Crystallography*[25]	
anomalous dispersion	*Int. Tables for X-Ray Crystallography*[25]	

PRECISE keyword was used and full geometry optimization was carried out (with the Fletcher−Powell algorithm) with the only geometry constraints showed in Table 3. It was verified (FORCE command) that the ground states (compounds **1**, **IV**, and **V**) and some transition states (**1**, *cis*-rotation; **IV**, *cis*- and *trans*-rotations; **V**, *cis*- and *trans*-rotations) correspond to none and one imaginary frequencies. The inversion values (compounds **1**, **IV**, and **V**) correspond to two imaginary frequencies (transition states of second order) and could be visualized as the transition state between the *cis*- and *trans*-rotations. It has been reported[6] that the transition states of carbodiimide itself **V** have one or two imaginary frequencies depending on the level of the calculations.

2-Nitrophenylacetaldehyde. To a solution of 2-nitrophenethyl alcohol (2 g, 12 mmol) in 50 mL of dry dichloromethane was added PCC (4.6 g, 20 mmol). The resultant mixture was well-stirred at room temperature for 3 h and filtered over $MgSO_4$. The filtrate was concentrated to dryness under reduced pressure and the residual material was purified by column chromatography (silica gel, dichloromethane) to give 2-nitrophenylacetaldehyde as a viscous oil in 71% yield: IR (Nujol) 1725, 1532, 1352, 718 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 4.13 (d, 2H, J = 0.9 Hz), 7.32 (dd, 1H, J = 7.6, 1.3 Hz), 7.49 (dd, 1H, J = 7.9, 1.3 Hz), 7.62 (td, 1H, J = 7.5, 1.3 Hz), 8.11 (dd, 1H, J = 0.9 Hz), 9.82 (t, 1H, J = 0.9 Hz); ^{13}C-NMR ($CDCl_3$) δ 48.4, 125.2, 128.4, 128.8, 133.5, 133.8, 148.3, 196.5; mass spectrum (relative intensity) 165 (M^+, 15), 149 (57), 136 (94), 120 (100). Anal. Calcd for $C_8H_7NO_3$: C, 58.18; H, 4.27; N, 8.48. Found: C, 58.39; H, 4.08; N, 8.25.

Preparation of Dinitroderivatives 10a and 10b. To a solution of (2-nitrobenzyl)triphenylphosphonium bromide (prepared in the usual way from 2-nitrobenzyl bromide) (15 g, 30 mmol) in 100 mL of dry dicloromethane were added 30 mmol of 2-nitrobenzaldehyde or 2-nitrophenylacetaldehyde, potassium carbonate (5.07 g, 40 mmol), and a few crystals of dibenzo-18-crown-6. The mixture was stirred at room temperature under nitrogen for 16 h. The precipitated solid was separated by filtration, and the filtrate was concentrated to dryness. The resultant solid was washed with ethanol and air-dried to give 2,2′-dinitrostilbene **10a**, as a mixture of *E* and *Z* isomers (1:3) as revealed by ^{1}H-NMR, in 95% yield or purified by column chromatography (silica gel, dichloromethane) to give 1,3-bis(2-nitrophenyl)propene **10b** in 65% yield as a mixture of *E* and *Z* isomers (1:1.7) as revealed by ^{1}H-NMR. **10a**: IR (Nujol) 1604, 1572, 1515, 1349 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 7.02 (dd, 2H*(Z)*, J = 7.5, 1.8 Hz), 7.10 (s, 2H*(Z)*), 7.29 (td, 2H*(Z)*, J = 7.3, 1.6 Hz), 7.37 (td, 2H*(Z)*, J = 7.3, 1.6 Hz), 8.07 (dd, 2H*(Z)*, J = 7.6, 1.6 Hz); ^{13}C-NMR ($CDCl_3$) δ 124.7*(Z)*, 128.5*(Z)*, 128.9*(Z)*, 132.5*(Z)*, 132.6*(Z)*, 133.2*(Z)*, 148.3*(Z)*; mass spectrum (relative intensity) 270 (M^+, 20), 165 (57), 135 (65), 92 (100). Anal. Calcd for $C_{14}H_{10}N_2O_4$: C, 62.22; H, 3.73; N, 10.37. Found: C, 62.49; H, 3.48; N, 10.13. **10b**: IR (Nujol) 1609, 1530, 1351, 745 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 3.73 (dd, 1.2H*(Z)*, J = 7.3, 1.6 Hz), 3.89 (dd, 0.8H*(E)*, J = 6.8, 1.3 Hz), 5.97 (dt, 0.6H*(Z)*, J = 11.5, 7.3 Hz), 6.36 (dt, 0.4H*(E)*, J = 15.7, 6.8 Hz), 6.91−6.97 (m, 0.6H*(Z)*), 7.29−7.64 (m, 3.6H*(Z)* + 3.2H*(E)*), 7.88−7.93 (m, 0.6H*(Z)*), 7.97 (dd, 0.4H*(E)*, J = 8.1, 1.3 Hz), 8.07 (dd, 0.6H*(Z)* J = 8.1, 1.3 Hz); ^{13}C-NMR ($CDCl_3$) δ 31.4, 36.5, 124.5, 124.7, 124.8, 124.9, 127.5, 127.7, 127.8, 128.0, 128.2, 128.4, 128.8, 129.6, 131.3, 131.6, 132.1, 132.2, 132.3, 132.5, 132.8, 133.1, 133.2, 133.3, 133.4, 134.4, 134.7, 148.2, 149.1 one methine carbon was not observed; mass spectrum (relative intensity) 220 (100), 189 (52), 132 (64), 92 (94). Anal. Calcd for $C_{15}H_{12}N_2O_4$: C, 63.38; H, 4.25; N, 9.85. Found: C, 63.01; H, 4.42; N, 10.01.

(*E*)-2,2′-Dinitrostilbene (11). To a solution of the mixture of *E* and *Z* isomers (1:3) of 2,2′-dinitrostilbene (**10a**, 1g, 3.7 mmol) in 30 mL of dry benzene was added thiophenol (0.21 g, 1.9 mmol). The resultant mixture was heated at reflux temperature and azoisobutyronitrile (0.81 g, 4.8 mmol) was added in three portions over a period of 5 h. The reaction mixture was stirred at this temperature overnight. After cooling, the solvent was removed under reduced pressure and the residual material was treated with ethanol, and the precipitated solid was filtered and air-dried to give (*E*)-2,2′-dinitrostilbene in 80% yield: mp 176−178 °C, yellow prisms (dichloromethane); IR (Nujol) 1517, 1447, 1356, 747 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 7.48 (td, 2H, J = 7.7, 1.5 Hz), 7.57 (s, 2H), 7.67 (td, 2H, J = 7.6, 1.3 Hz), 7.82 (dd, 2H, J = 7.9, 1.5 Hz), 8.04 (dd, 2H, J = 8.1, 1.3 Hz); ^{13}C-NMR ($CDCl_3$) δ 125.0, 128.9, 129.0, 129.2, 132.6, 133.7, 147.9; mass spectrum (relative intensity) 270 (M^+, 9), 151 (53), 135 (69), 92 (100). Anal. Calcd for $C_{14}H_{10}N_2O_4$: C, 62.22; H, 3.73; N, 10.37. Found: C, 62.56; H, 3.59; N, 10.60.

Preparation of (*E*)- and (*Z*)-2,2′-diaminostilbene (15). To a well stirred mixture of (*Z*)-2,2′-dinitrostilbene (**10a**, *E*/*Z* 1:3) or (*E*)-2,2′-dinitrostilbene (**11**, 13 mmol) in 85 mL of ethanol were added 85 mL of glacial acetic acid and reduced iron powder (14.5 g, 260 mmol). The reaction mixture was heated at reflux temperature for 3 h. After cooling, the mixture was poured into water (200 mL) and neutralized with Na_2CO_3. The resultant mixture was extracted with ether (3 × 250 mL) and the combined organic layers were washed with water (250 mL) and dried over $MgSO_4$. The solvent was removed under reduced presure and the resultant solid was recrystalized from chloroform/*n*-hexane to give respectively *Z*-**15** (*E*/*Z* 1:3) in 90% yield or *E*-**15** in 92% yield. *Z*-**15**: IR (Nujol) 1613, 1491, 1455, 751 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 3.63 (s, 4H), 6.53−6.63 (m, 6H), 6.97−7.05 (m, 4H); ^{13}C-NMR ($CDCl_3$) δ 115.8, 118.3, 122.6, 127.1, 128.5, 129.6, 143.8; mass spectrum (relative intensity) 211 (M^+ + 1, 21), 210 (M^+, 100), 209 (72), 193 (55). Anal. Calcd for $C_{14}H_{14}N_2$: C, 79.97; H, 6.71; N, 13.32. Found: C, 80.12; H, 6.98;N, 13.05. *E*-**15**: Mp 179−181 °C, pale yellow prisms (chloroform); IR (Nujol) 1623, 1575, 1501, 759 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 3.59 (s, 4H), 6.71 (d, 2H, J = 8.1 Hz), 6.80 (t, 2H, J = 7.4 Hz), 7.02 (s, 2H), 7.10 (t, 2H, J = 7.4 Hz), 7.39 (d, 2H, J = 7.6 Hz); ^{13}C-NMR ($CDCl_3$) δ 116.2, 119.3, 124.2, 126.0, 127.3, 128.7, 144.0; mass spectrum (relative intensity) 210 (M^+, 100), 209 (52), 193 (62), 118 (48). Anal. Calcd for $C_{14}H_{14}N_2$: C, 79.97; H, 6.71; N, 13.32. Found: C, 80.09; H, 6.91; N, 13.44.

Preparation of the Diamines 7 And 19. To a solution of the appropriate dinitro compound **6** or **10b** (7.04 mmol) in 50 mL of ethanol was added 0.2 g of Pd on charcoal (10%), and the reaction mixture was stirred at room temperature under hydrogen for 7 or 3 h, respectively. Then, the mixture was filtered over celite. The filtrate was concentrated to dryness under reduced pressure and the resultant materials were chromatographed to give the corresponding diamine:

7: (Silica gel, diethyl ether) 89% yield; yellow oil; IR (Nujol) 3357, 1623, 1501, 1454 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 1.27 (d, 3H, J = 6.8 Hz), 2.66 (dd, 1H, J = 13.9, 8.0 Hz), 2.89 (dd, 1H, J = 13.9, 5.9 Hz), 3.18−3.29 (m, 1H), 4.87 (s, broad, 4H), 6.72−6.80 (m, 3H), 6.89 (td, 1H, J = 7.3, 1.1 Hz), 6.95−7.04 (m, 3H), 7.23 (dd, 1H, J = 7.6, 1.5 Hz); ^{13}C-NMR ($CDCl_3$) δ 20.0, 32.4, 40.2, 116.1, 116.6, 118.9, 119.6, 122.5, 126.0, 126.8, 127.3, 131.1, 132.1, 143.6, 144.3 ; mass spectrum (relative intensity) 226 (M^+, 12), 121 (10), 120 (100), 106 (20). Anal. Calcd for $C_{15}H_{18}N_2$: C, 79.81; H, 8.02; N, 12.38. Found: C, 80.03; H, 7.69; N, 12.57.

19: (Silica gel, *n*-hexane/ethyl acetate 1:1) 90% yield; mp 215−217 °C, colorless prisms; IR (Nujol) 1572, 1542, 1495, 744 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 1.75−1.95 (m, 2H), 2.67−2.74 (m, 4H), 4.25 (s, broad, 4H), 7.06−7.23 (m, 8H); ^{13}C-NMR ($CDCl_3$) δ 30.4, 30.5, 121.1, 124.8, 127.0, 130.1, 132.9, 134.8 ; mass spectrum (relative intensity) 226 (M^+, 61), 120 (100), 107 (56), 106 (85). Anal. Calcd for $C_{15}H_{18}N_2$: C, 79.81; H, 8.02; N, 12.38. Found: C, 79.99; H, 8.30; N, 12.14.

Preparation of Diazides 8, 12, 16, and 20. To a cooled (0 °C) solution of the appropriate diamine (7.5 mmol) in 2 N HCl (52 mL) was added dropwise a solution of sodium nitrite (1.3 g, 19 mmol) in 10 mL of water. The resultant solution was stirred at 0 °C for 1 h. A solution of sodium azide (2.1g, 32 mmol) in 15 mL of water was then added dropwise, and the reaction mixture was allowed to warm at room temperature. The resultant mixture was extracted with ether (3 × 60 mL), and the combined organic layers were washed with water (75 mL) and dried over $MgSO_4$. The solvent was removed under reduced pressure and the residual material was purified by column chromatography to give the corresponding diazide:

8: (Silica gel, *n*-hexane/diethyl ether 7:3); 95% yield; pale yellow oil; IR (Nujol) 2127, 1586, 1491, 1294 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 1.18 (d, 3H, J = 6.9 Hz), 2.79 (d, 2H, J = 7.6 Hz), 3.35−3.49 (m, 1H), 6.96−7.29 (m, 8H); ^{13}C-NMR ($CDCl_3$) δ 20.2, 34.1, 38.5, 118.0, 118.1, 124.4, 124.9, 127.1, 127.5, 127.6, 131.2, 132.1, 137.6, 138.0, 138.4; mass spectrum (relative intensity) 278 (M^+, 43), 221 (78), 207 (67), 77 (100). Anal. Calcd for $C_{15}H_{14}N_6$: C, 64.73; H, 5.07; N, 30.20. Found: C, 64.53; H, 5.22; N, 30.01.

12: (Silica gel, *n*-hexane/diethylether 7:3); 94% yield; mp 142−144 °C, pale yellow prisms ; IR (Nujol) 2137, 1490, 1453, 1310 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 7.09−7.17 (m, 4H), 7.23−7.34 (m, 4H), 7.36 (dd, 2H, J = 7.5, 1.5 Hz); ^{13}C-NMR ($CDCl_3$) δ 118.6, 124.5, 125.0, 126.7, 129.0, 129.1, 137.5; mass spectrum (relative intensity) 262 (M^+, 6), 205 (38), 204 (100), 178 (41). Anal. Calcd for $C_{14}H_{10}N_6$: C, 64.11; H, 3.84; N, 32.04. Found: C, 63.89; H, 3.62; N, 31.79.

16: (Silica gel, petroleum ether/diethyl ether 7:3); 96% yield (*E*/*Z* 1:3) as revealed by ^{1}H-NMR; mp 106−108 °C; IR (Nujol) 2130, 1478, 1307, 1285 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 6.68 (s, 2H), 6.86 (td, 2H, J = 7.5, 1.1 Hz), 7.03 (dd, 2H, J = 7.6, 1.4 Hz), 7.13 (dd, 2H, J = 8.1, 1.1 Hz), 7.23 (td, 2H, J = 7.6, 1.5 Hz); ^{13}C-NMR ($CDCl_3$) δ 118.4, 124.4, 126.8, 128.7, 128.8, 130.4, 138.2; mass spectrum (relative intensity) 262 (M^+, 33), 206 (42), 205 (100), 179 (24). Anal. Calcd for $C_{14}H_{10}N_6$: C, 64.11; H, 3.84; N, 32.04. Found: C, 64.35; H, 4.03; N, 32.17.

20: (Silica gel, *n*-hexane/diethyl ether 7:3); 80% yield; yellow oil; IR (Nujol) 2122, 1491, 1289, 748 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 1.78−1.88 (m, 2H), 2.60 (t, 4H, J = 7.8 Hz), 7.04 (td, 2H, J = 7.4, 1.3 Hz), 7.10 (dd, 2H, J = 8.1, 1.0 Hz), 7.15 (dd, 2H, J = 7.6, 1.3 Hz), 7.21 (td, 2H, J = 7.5, 1.6 Hz); ^{13}C-NMR ($CDCl_3$) δ 30.7, 31.1, 118.1, 124.7, 127.3, 130.4, 133.7, 138.0; mass spectrum (relative intensity) 278 (M^+, 19), 193 (55), 118 (100), 77 (50). Anal. Calcd for $C_{15}H_{14}N_6$: C, 64.73; H, 5.07; N, 30.20. Found: C, 64.97; H, 5.32; N, 30.04.

Preparation of *cis*- and *trans*-2,2′-Diazidostilbene Oxides (Epoxides 13 and 17). To a solution cooled at 0 °C of (*E*)-2,2′-diazidostilbene (**12**) or (*Z*)-2,2′-diazidostilbene (**16**, *E*/*Z* 1:3) (2 g, 7 mmol) in 50 mL of dry dichloromethane was added *m*-CPBA (50−60%) (1.97 g). The resultant mixture was stirred at 0 °C for 3 h. A second portion of *m*-CPBA (1.97 g) was then added. The reaction mixture was allowed to warm at room temperature and stirred overnight. A saturated aqueous solution of $NaHCO_3$ (30 mL) was added. The organic layer was separated, washed with water, and dried over $MgSO_4$. The solvent was removed under reduced pressure, and the residual material was purified by column chromatography to give respectively *trans*-2,2′-diazidostilbene oxide (**13**, silica gel, dichloromethane) or *cis*-2,2′-diazidostilbene oxide (**17**, silica gel, *n*-hexane/dichloromethane 4:1).

13: 72% yield; mp 124−126 °C, yellow prisms; IR (Nujol) 2129, 1499, 1298, 752 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 3.94 (s, 2H), 7.05−7.16 (m, 4H), 7.21−7.33 (m, 4H); ^{13}C-NMR ($CDCl_3$) δ 58.1, 116.0, 125.1, 125.7, 128.3, 129.3, 138.7; mass spectrum (relative intensity) 220 (16), 193 (85), 91 (82), 75 (100). Anal. Calcd for $C_{14}H_{10}N_6O$: C, 60.43; H, 3.62; N, 30.20. Found: C, 60.13; H, 3.99; N, 30.03.

17: 42% yield; mp 117−119 °C, yellow prisms; IR (Nujol) 2130, 1493, 1296, 764 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 4.42 (s, 2H), 6.88−7.01 (m, 4H), 7.12−7.25 (m, 4H); ^{13}C-NMR ($CDCl_3$) δ 57.0, 117.6, 124.0, 125.6, 128.2, 128.8, 138.3; mass spectrum (relative intensity) 221 (38), 194 (100), 193 (59), 92 (25). Anal. Calcd for $C_{14}H_{10}N_6O$: C, 60.43; H, 3.62; N, 30.20. Found: C, 60.16; H, 3.35; N, 29.98.

Preparation of Bis(iminophosphoranes) 9, 14, 18, and 21. To a solution of the appropriate diazide **8**, **13**, **17**, or **20** (3 mmol) in 30 mL of dry diethyl ether was added triphenylphos-

phane (1.6 g, 6 mmol). The resultant mixture was stirred at room temperature for 6 h. The precipitated solid was collected by filtration and air-dried to give the corresponding bis-(iminophosphorane).

9: 82% yield; mp 214−216 °C, pale yellow needles (diethyl ether); IR (Nujol) 1487, 1444, 1352, 1113 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 1.32 (d, 3H, J = 7.1 Hz), 3.33 (d, 2H, J = 7.4 Hz), 4.21−4.32 (m, 1H), 6.43−6.49 (m, 2H), 6.54 (td, 1H, J = 7.4, 0.8 Hz), 6.62−6.76 (m, 3H), 7.27−7.42 (m, 20 H), 7.69−7.82 (m, 12H); ^{13}C-NMR ($CDCl_3$) δ 20.3, 34.9, 38.7, 117.0, 117.4, 120.9 (d, $^3J_{C-P}$ = 10.0 Hz), 121.12 (d, $^3J_{C-P}$ = 10.1 Hz), 125.1, 125.3, 126.4 (d, $^4J_{C-P}$ = 2.1 Hz), 128.4 (d, $^3J_{C-P}$ = 11.7 Hz), 128.4 (d, $^3J_{C-P}$ = 12.1 Hz), 129.9 (d, $^4J_{C-P}$ = 1.8 Hz), 131.3 (d, $^4J_{C-P}$ = 2.7 Hz, two carbons), 131.9 (d, $^1J_{C-P}$ = 99.1 Hz, two carbons), 132.6 (d, $^2J_{C-P}$ = 9.5 Hz, two carbons), 137.0 (d, $^3J_{C-P}$ = 22.0 Hz), 142.9 (d, $^3J_{C-P}$ = 22.0 Hz), 148.6, 149.4; ^{31}P-NMR δ ($CDCl_3$) −1.63, −0.87; mass spectrum (relative intensity) 487 (1), 183 (26), 86 (49), 84 (100). Anal. Calcd for $C_{51}H_{44}N_2P_2$: C, 82.02 H, 5.94; N, 3.75. Found: C, 81.68; H, 5.67; N, 3.57.

14: 95% yield; mp 176−178 °C, white needles (diethyl ether); IR (Nujol) 1480, 1437, 1114, 722 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 4.79 (s, 2H), 6.43 (d, 2H, J = 7.6 Hz), 6.73 (t, 2H, J = 7.3 Hz), 6.88 (td, 2H, J = 7.5, 1.5 Hz), 7.01−7.11 (m, 10H), 7.21−7.47 (m, 10H), 7.54−7.65 (m, 12H); ^{13}C-NMR ($CDCl_3$) δ 61.9, 117.2, 120.3 (d, $^3J_{C-P}$ = 9.6 Hz),124.0 (d, $^4J_{C-P}$ = 2.7 Hz), 127.0, 128.3 (d, $^3J_{C-P}$ = 12.1 Hz), 131.2 (d, $^4J_{C-P}$ = 2.9 Hz), 131.3 (d, $^1J_{C-P}$ = 100.0 Hz), 132.5 (d, $^2J_{C-P}$ = 9.6 Hz), 132.8 (d, $^3J_{C-P}$ = 21.1 Hz), 149.7; ^{31}P-NMR δ ($CDCl_3$) −1.83; mass spectrum (relative intensity) 469 (29), 468 (100), 467 (27), 183 (31). Anal. Calcd for $C_{50}H_{40}N_2OP_2$: C, 80.41; H, 5.40; N, 3.75. Found: C, 80.14; H, 5.18; N, 4.02.

18: 80% yield; mp 122−124 °C dec; yellow needles (diethyl ether); IR (Nujol) 1597, 1448, 1334, 1110 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 5.30 (s, 2H), 6.24 (t, 2H, J = 7.8 Hz), 6.43 (t, 2H, J = 7.3 Hz), 6.67 (td, 2H, J = 7.5, 1.4 Hz), 7.09−7.33 (m, 20H), 7.56−7.66 (m, 12H); ^{13}C-NMR ($CDCl_3$) δ 59.7, 116.1, 120.3 (d, $^3J_{C-P}$ = 11.2 Hz),126.9, 127.9 (d, $^4J_{C-P}$ = 2.4 Hz), 128.4 (d, $^3J_{C-P}$ = 12.0 Hz), 129.4 (d, $^3J_{C-P}$ = 21.1 Hz), 131.2 (d, $^4J_{C-P}$ = 2.8 Hz), 131.3 (d, $^1J_{C-P}$ = 99.1 Hz), 132.6 (d, $^2J_{C-P}$ = 9.6 Hz), 150.5; ^{31}P-NMR δ ($CDCl_3$) 0.47; mass spectrum (relative intensity) 468 (4), 206 (47), 205 (35), 183 (100). Anal. Calcd for $C_{50}H_{40}N_2OP_2$: C, 80.41; H, 5.40; N, 3.75. Found: C, 80.75; H, 5.14; N, 3.42.

21: 87% yield; mp 198−200 °C, colorless prisms (diethyl ether); IR (Nujol) 1482, 1452, 1348, 1111 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 2.09−2.19 (m, 2H), 3.06 (t, 4H, J = 7.7 Hz), 6.46 (d, 2H, J = 7.6 Hz), 6.56 (d, 2H, J = 7.3 Hz), 6.72 (td, 2H, J = 7.6, 1.6 Hz), 7.04−7.09 (m, 2H), 7.31−7.46 (m, 18H), 7.72−7.79 (m, 12H) ; ^{13}C-NMR ($CDCl_3$) δ 30.0, 33.6, 117.2, 121.0 (d, $^3J_{C-P}$ = 9.6 Hz), 121.5, 128.5 (d, $^3J_{C-P}$ = 11.6 Hz), 129.3 (d, $^4J_{C-P}$ = 2.0 Hz), 131.4 (d, $^4J_{C-P}$ = 3.0 Hz), 131.9 (d, $^1J_{C-P}$ = 99.2 Hz), 132.6 (d, $^2J_{C-P}$ = 9.6 Hz), 137.6 (d, $^3J_{C-P}$ = 21.6 Hz), 148.5; ^{31}P-NMR δ ($CDCl_3$) −0.85; mass spectrum (relative intensity) 380 (21), 183 (97), 120 (100), 108 (51). Anal. Calcd for $C_{51}H_{44}N_2P_2$: C, 82.02; H, 5.94; N, 3.75. Found: C, 81.77; H, 5.67; N, 3.99.

(*E*)-2,3-Bis(2-nitrophenyl)propenol (5). To a stirred solution of $NaBH_4$ (0.79 g, 21 mmol) in 25 mL of dry 1,2-dimethoxyethane at 0 °C under nitrogen was added dropwise titanium tetrachloride (0.76 mL, 7 mmol). The resultant mixture was stirred 10 min and then a solution of (*E*)-2,3-bis(*2*-nitrophenyl)propenoic acid[27] in 7 mL of dry 1,2-dimethoxyethane was added dropwise. The resultant mixture was stirred overnight. The reaction mixture was cooled at 0 °C, and water was added slowly and then the whole mixture was extracted with diethyl ether. The combined organic layer was washed with water and dried over $MgSO_4$. The solvent was removed under reduced pressure, and the resultant material was purified by column chromatography (silica gel, diethyl ether/*n*-hexane 7:3) to give **5** as a yellow oil in 55% yield: IR (Nujol) 3405, 1542, 1523, 1353 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 2.65 (s, 1H), 4.47 (s, 2H), 7.01−7.04 (m, 1H), 7.13 (s, 1H), 7.17 (dd, 1H, J = 7.6, 1.6 Hz), 7.24−7.29 (m, 2H), 7.34−7.41 (m, 1H), 7.42−7.48 (m, 1H), 7.91−7.97 (m. 2H); ^{13}C-NMR ($CDCl_3$) δ 66.5, 124.2, 124.4, 124.6, 128.0, 128.8, 131.5, 132.2, 132.4, 132.9, 133.4, 133.6, 141.9, 148.1, 148.7; mass spectrum (relative intensity) 283 (1), 269 (1), 135 (75), 104 (87), 92 (100). Anal. Calcd for $C_{15}H_{12}N_2O_5$: C, 60.00; H, 4.03; N, 9.33. Found: C, 59.76; H, 4.21; N, 9.65.

(*E*)-2,3-Bis(2-nitrophenyl)propenyl Methanesulfonate. To a solution of (*E*)-2,3-bis(2-nitrophenyl)propenol (**5**, 0.31g, 1 mmol) and triethylamine (0.16 g, 1.55 mmol) in 10 mL of dry THF at 0 °C under nitrogen was added dropwise a solution of methanesulfonyl chloride (0.18 g, 1.55 mmol). The reaction mixture was stirred and allowed to warm up at room temperature. After 3 h the precipitated triethylammoniun chloride was separated by filtration. The filtrate was concentrated to dryness under reduced pressure, and the resultant material was purified by column chromatography (silica gel, diethyl ether/*n*-hexane 4:1) to give (*E*)-2,3-bis(2-nitrophenyl)propenyl methanesulfonate in 97% yield: mp 106−108 °C, colorless prisms (diethyl ether/*n*-hexane); IR (Nujol) 1528, 1340, 1178, 950 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 3.04 (s, 3H), 5.11 (s, 2H), 6.98−7.03 (m, 1H), 7.16−7.21 (m, 1H), 7.27 (s, 1H), 7.30−7.35 (m, 2H), 7.43−7.49 (m, 2H), 7.99−8.07 (m, 2H); ^{13}C-NMR ($CDCl_3$) δ 37.9, 72.2, 124.7, 124.9, 128.9, 129.6, 129.8, 131.2, 131.3, 131.6, 133.0, 133.4, 133.9, 134.8, 147.8, 148.4; mass spectrum (relative intensity) 203 (1), 206 (42), 135 (54), 134 (100). Anal. Calcd for $C_{16}H_{14}N_2O_7S$: C, 50.79; H, 3.73; N, 7.40. Found: C, 50.89; H, 3.55; N, 7.57.

1,2-Bis(2-nitrophenyl)propene (6). To a solution of (*E*)-2,3-bis(2-nitrophenyl)propenyl methanesulfonate (0.57 g, 1.51 mmol) in 23 mL of HMPA and 5.7 mL of water was added $NaBH_4$ (0.23g, 6.03 mmol), and the reaction mixture was stirred for 15 min; afterward water (25 mL) was added, and the resultant mixture was stirred for 10 min and extracted with diethyl ether (50 mL), and the organic layer was separated, washed with water (2 × 40 mL) and dried over $MgSO_4$. The solvent was removed under reduced pressure and the resultant material was chromatographed (silica gel, diethyl ether/*n*-hexane 3:2) to give **6** in 75% yield as a mixture of *E* and *Z* isomers (4:1) as revealed by ^{1}H-NMR: IR (Nujol) 1613, 1581, 1527, 1347 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 2.00 (d, 0.6H*(Z)*, J = 1.8 Hz), 2.19 (d, 2.4H*(E)*, J = 1.6 Hz), 6.67−6.69 (d, 0.2H*(Z)*, J = 1.8 Hz), 6.84−6.86 (m, 0.8H*(E)*, J = 1.6 Hz), 7.00−7.97 (m, 6.4H*(E)* + 1.2H*(Z)*), 7.99 (dd, 0.2H*(Z)*, J = 8.1, 1.3 Hz), 8.10 (dd, 0.2H*(Z)*, J = 8.4, 1.3 Hz); ^{13}C-NMR ($CDCl_3$) δ 20.6*(Z)*, 24.7*(E)*, 124.1*(E)*, 124.4*(E)*, 124.5*(E)*, 124.6*(Z)*, 125.5*(Z)*, 127.6*(E)*, 128.1*(Z)*, 128.2*(E)*, 130.8*(Z)*, 131.5*(E)*, 131.8*(E)*, 132.1*(Z)*, 132.6*(Z)*, 132.7*(E)*, 132.9*(E)*, 133.2*(Z)*, 133.3*(Z)*, 133.6*(E)*, 137.1*(E)*, 137.5*(Z)*, 138.5*(E)*, 139.7*(Z)*, 147.8*(Z)*, 148.0*(Z)*, 148.1*(E)*, 148.2*(E)*, two methine carbons were not observed; mass spectrum (relative intensity) 241 (8), 136 (52), 135 (100), 104 (72). Anal. Calcd for $C_{15}H_{12}N_2O_4$: C, 63.38; H, 4.25; N, 9.85. Found: C, 63.55; H, 4.08; N, 10.01.

Preparation of Bis(isothiocyanates). To a solution of the appropriate bis(iminophosphorane) **9**, **14**, **18**, or **21** (1.04 mmol) in 30 mL of dry benzene was added an excess of carbon disulfide (3 mL), and the resultant mixture was stirred under nitrogen at reflux temperature for 4 h. After cooling the solvent was removed under reduced pressure, and the crude material was chromatographed to give the corresponding bis-(isothiocyanate).

2,2′-Propylene-1,1′-bis(phenyl isothiocyanate): (Silica gel, *n*-hexane/dichloromethane 1:1); 97% yield; colorless oil; IR (Nujol) 2100, 1491, 1448, 759 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 1.34 (d, 3H, J = 7.0 Hz), 2.84 (dd, 1H, J = 13.4, 8.1 Hz), 3.01 (dd, 1H, J = 13.4, 6.9 Hz), 3.35−3.53 (m, 1H), 6.00−7.35 (m, 8H); ^{13}C-NMR ($CDCl_3$) δ 20.2, 36.1, 40.0, 126.6, 126.8, 127.0, 127.2, 127.3, 127.4, 127.7, 129.4, 130.2, 130.6, 134.9, 135.2, 136.1, 141.3; mass spectrum (relative intensity) 310 (M^+, 45), 162 (100), 128 (98), 77 (21). Anal. Calcd for $C_{17}H_{14}N_2S_2$: C, 65.78; H, 4.55; N, 9.02. Found: C, 65.95; H, 4.34; N, 9.17.

2,2′-(*trans*-Oxirane-2,3-diyl)-1,1′-bis(phenyl isothiocyanate): (Silica gel, *n*-hexane/dichloromethane 1:1) 52%; mp 121−123 °C, colorless prisms; IR (Nujol) 2111, 1485, 1458, 755 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 4.08 (s, 2H), 7.28−7.39 (m, 8H); ^{13}C-NMR ($CDCl_3$) δ 58.8, 125.5, 126.8, 127.8, 129.4, 130.6, 132.4,

(27) Pailer, M.; Schleppnick, A.; Meller, A. *Monatsh. Chem.* **1958**, *89*, 211.

(28) The author has deposited atomic coordinates for **2** and **3** with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK.

138.6; mass spectrum (relative intensity) 310 (M^+, 2), 179 (47), 146 (62), 120 (100). Anal. Calcd for $C_{16}H_{10}N_2OS_2$: C, 61.91; H, 3.25; N, 9.03. Found: C, 62.07; H, 3.06; N, 8.87.

2,2′-(*cis*-Oxirane-2,3-diyl)-1,1′-bis(phenyl isothiocyanate): (Silica gel, *n*-hexane/dichloromethane 1:1) 55% yield; mp 73−75 °C, colorless prisms; IR (Nujol) 2074, 1603, 1385, 754 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 4.59 (s, 2H), 7.03−7.17 (m, 8H); ^{13}C-NMR ($CDCl_3$) δ 57.3, 126.5, 126.6, 127.8, 128.9, 129.8, 130.3, 138.6; mass spectrum (relative intensity) 310 (M^+, 4), 179 (54), 146 (60), 120 (100). Anal. Calcd for $C_{16}H_{10}N_2OS_2$: C, 61.91; H, 3.25; N, 9.03. Found: C, 61.75; H, 3.12; N, 9.21.

2,2′-Trimethylene-1,1′-bis(phenyl isothiocyanate): (Silica gel, *n*-hexane/dichloromethane 4:1) 77% yield; colorless oil; IR (Nujol) 2095, 1491, 1454 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 1.87−1.98 (m, 2H), 2.77 (t, 4H, J = 7.7 Hz), 7.17−7.25 (m, 8H); ^{13}C-NMR ($CDCl_3$) δ 30.6, 32.0, 126.5, 127.3, 127.6, 130.1, 135.6, 137.1, 138.4; mass spectrum (relative intensity) 312 (M^+ + 2, 8), 311 (M^+ + 1, 17), 310 (M^+, 90), 252 (100). Anal. Calcd for $C_{17}H_{14}N_2S_2$: C, 65.78; H, 4.55; N, 9.02. Found: C, 65.86; H, 4.60; N, 9.18.

Preparation of Bis(carbodiimides) 22, 23, 25, and 26. Method A: To a solution of the appropriate bis(iminophosphorane) **9**, **14**, **18**, or **21** (0.69 mmol) in 20 mL of dry dichloromethane was added Boc_2O (0.3 g, 1.39 mmol), except for the bis(iminophosphorane) **9** which requires 5 equiv of Boc_2O, and DMAP (0.083 g, 0.69 mmol). The resultant mixture was stirred under nitrogen at room temperature for 12 h. The solvent was removed under reduced pressure and the resultant material was chromatographed to give the corresponding bis(carbodiimide).

Method B: To a solution of the appropriate bis(iminophosphorane) **9**, **14**, **18**, or **21** (0.33 mmol) in 20 mL of dry benzene was added an excess of solid carbon dioxide. The mixture was heated in a glass sealed tube at 70 °C for 16 h. After cooling, the solvent was removed under reduced pressure, and the remaining material was chromatographed to give the corresponding bis(carbodiimide).

Method C: To a solution of the appropriate bis(isothiocyanate) (0.7 mmol) in 30 mL of dry benzene was added the corresponding bis(iminophosphorane) (0.7 mmol). The reaction mixture was stirred at reflux temperature under nitrogen for 24 h. After cooling, the solvent was removed under reduced pressure and the residue was chromatographed to give the corresponding carbodiimide.

22: (Silica gel, *n*-hexane/dichloromethane 3:2) 98% yield (method B); mp 89−91 °C, colorless prisms (*n*-hexane); IR (Nujol) 2121, 1590, 1454, 759 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 1.44 (d, 3H, J = 6.4 Hz), 2.37 (dd, 1H, J = 15.2, 8.3 Hz), 3.50−3.65 (m, 2H), 6.98−7.27 (m, 7H), 7.35 (dd, 1H, J = 7.2, 1.9 Hz); ^{13}C-NMR ($CDCl_3$) δ 18.5, 35.0, 42.7, 123.4, 123.5, 125.0, 125.1, 125.8, 127.5, 128.1, 130.6, 134.2, 138.4, 138.7, 139.2, 142.8; HRMS (EI) M^+ 234.1158, theor 234.1157. Anal. Calcd for $C_{16}H_{14}N_2$: C, 82.02; H, 6.02; N, 11.96. Found: C, 81.88; H, 5.85; N, 12.06.

23: (Silica gel, petroleum ether/dichloromethane 1:1) 21% yield (method A); mp 226−228 °C, colorless prisms (chloroform); IR (Nujol) 2159, 1484, 1454, 757 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 4.04 (s, 4H), 6.93−6,96 (m, 4H), 7.05−7.11 (m, 8H), 7.30−7.33 (m, 4H); ^{13}C-NMR ($CDCl_3$) δ 59.5, 124.2, 125.0, 125.8, 129.1, 131.3, 135.2, 136.8; HRMS (EI) M^+ 468.1593, theor 468.1586. Anal. Calcd for $C_{30}H_{20}N_4O_2$: C, 76.91; H, 4.30; N, 11.96. Found: C, 77.07; H, 4.54; N, 11.75.

25 (Diastereoisomer more soluble in dichloromethane, remaining in solution): (Silica gel, *n*-hexane/diethyl ether 7:3) 10% yield; IR (Nujol) 2153, 1602, 1581, 1448 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 4.63 (s, 4H), 6.92−7.22 (m, 16H); ^{13}C-NMR ($CDCl_3$) δ 57.6, 123.9, 124.6, 127.9, 128.2, 128.6, 130.7, 136.6; Anal. Calcd for $C_{30}H_{20}N_4O_2$: C, 76.91; H, 4.30; N, 11.96. Found: C, 77.03; H, 4.47; N, 12.01.

25 (Diastereoisomer crystallized from dichloromethane): (Silica gel, *n*-hexane/diethyl ether 7:3) 10% yield; mp 248−250 °C, colorless prisms (dichoromethane); IR (Nujol) 2147, 1492, 1455, 751 cm^{-1}; ^{1}H-NMR (CDCl3) δ 4.61 (s, 4H), 6.92−7.00 (m, 8H), 7.10 (td, 4H, J = 7.6, 1.6), 7.18 (dd, 4H, J = 7.6, 1.6 Hz); ^{13}C-NMR ($CDCl_3$) δ 57.7, 124.1, 124.7, 128.0, 128.4, 128.5, 133.2, 136.8; HRMS (EI) M^+ 468.1574, theor 468.1586. Anal. Calcd for $C_{30}H_{20}N_4O_2$: C, 76.91; H, 4.30; N, 11.96. Found: C, 76.79; H, 4.22; N, 11.78.

26: (Silica gel, *n*-hexane/dichloromethane 7:3) 40% yield; mp 199−201 °C, colorless prisms (chloroform/*n*-hexane); IR (Nujol) 2143, 1581, 1491, 1384 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 1.88−199 (m, 4H), 2.79 (t, 8H, J = 8.0 Hz), 7.03−7.20 (m, 16H); ^{13}C-NMR ($CDCl_3$) δ 32.3, 33.2, 125.2, 125.4, 127.1, 130.2, 133.7, 136.9, 137.3; HRMS (EI) M^+ 468.2316, theor 468.2314. Anal. Calcd for $C_{32}H_{28}N_4$: C, 82.02; H, 6.02; N, 11.96. Found: C, 82.14; H, 6.23;N, 12.05.

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