

Conformational behaviour of 2,2'-bipyrrole

An *ab initio* approach

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The rotational potential around the interannular bond in 2,2'-bipyrrole has been calculated making use of standard minimal STO-3G and split valence 4-31G basis sets. Geometrical optimization concerning the most significant interannular internal parameters has been performed with both basis sets. The trans conformer is predicted to be more stable than the cis. The minimal basis set predicts the existence of a cisoid-gauche minimum which after limited optimization becomes very shallow and it seems to be an artifact of the rigid rotor approximation. At 4-31G level, both the trans and cis conformers represent maxima in the potential curve and two gauche minima appear at $\theta = 46.0^\circ$ and $\theta = 147.6^\circ$, the latter being the absolute minimum. The absolute maximum of the potential curve corresponds to the cis conformer.

Key words: 2,2'-Bipyrrole — Rotational barrier — MO calculations

1. Introduction

Recently, electrochemically synthesized polypyrrole [1] has been recognized as a potentially useful organic polymer, since it can be doped by electron acceptors (such as I_2 or AsF_5) to attain a conductivity which is almost comparable with that of metals [2-4]. Due to its high conductivity and much better environmental stability than other highly conducting polymers such as polyacetylene or polypara-phenylene, polypyrrole has been proposed in a great number of technological applications [5-9]. Thus, in the last years, the electronic structure of polypyrrole has been the subject of a variety of experimental (see [4] and [10-12] and references therein) and theoretical [13-18] works in order to better understand

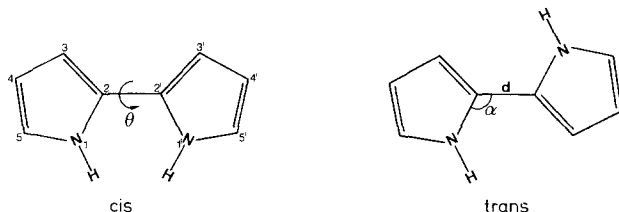


Fig. 1. Cis ($\theta = 0^\circ$) and trans ($\theta = 180^\circ$) structures of 2,2'-bipyrrole. Numbering and optimized internal parameters (d , α) are indicated

its electrical properties. However, present knowledge of the properties of polypyrroles, in particular the chemical and electronic structure, is far from complete.

Until now, all theoretical works dealing with polypyrrole have chosen to model the polymer as a planar linear chain molecule in which the orientation of the individual monomeric subunits alternate as one proceeds along the chain. However, it is very important to note the existence of a cis-trans conformational isomerism which should determine the flexibility of the polymer [19] and might condition its conductivity properties, e.g. it is well known that cis- and trans-polyacetylene exhibit different conductivities [20]. The aim of the present work is to study the cis-trans isomerization of the 2,2'-bipyrrole, which is usually taken as the unit cell for the polymer [13, 18], and to calculate the energy of the different conformeric structures using *ab initio* self-consistent-field method.

The conformational properties of 2,2'-bipyrrole have been the subject of some theoretical calculations at semiempirical level [21, 22]. Galasso et al. [21], using the EHT method, reported a very high barrier (about 9 kcal mol^{-1}) for the cis-trans interconversion with the trans conformation higher in energy. In a previous full geometry optimization study with the INDO approach [22], a cis minimum has been found $0.80 \text{ kcal mol}^{-1}$ higher than the trans minimum and separated from it by a barrier of $4.29 \text{ kcal mol}^{-1}$ (in contrast with EHT results). Recently, a X-ray diffraction study has been referenced by J. M. André et al. [18]. In this study, a planar trans conformation is reported for 2,2'-bipyrrole.

2. Computational method

The starting geometry for 2,2'-bipyrrole (see Fig. 1) was that of two fused single pyrrole rings at their experimental microwave geometry [23] and joined along the C-replaced H direction as it has been reported elsewhere for similar systems [24]. The initial inter-ring distance was 1.47 \AA , and the internal rotation coordinate was the dihedral angle θ .

Ab initio LCAO-MO calculations were performed using an amplified version of the GAUSSIAN-70 program [25] adapted to run on a SPERRY-1100/81 computer. Computations were carried out at both the minimal STO-3G [26] and the split valence 4-31G [27] basis set levels. To avoid a heavy full optimization, we have taken advantage of the well-known fact that, in conformational studies

implying generalized geometry optimization, displacement along the rotation coordinate mainly affects the internal parameters in the environment of the twisting bond [28–31]. Hence, only the internal parameters shown in Fig. 1 have been optimized. In this way we expect to avoid the rough approximation involved in the rigid rotor model and computation timing can be held within reasonable limits.

The energy values at $\theta = 0, 30, 60, 90, 120, 150$ and 180° have been used to fit the potential function by means of a truncated Fourier expansion

$$V(\phi) = \sum_{i=1}^6 1/2 V_i (1 - \cos i\phi)$$

In this expression V is the relative energy at the torsional angle ϕ which is related to θ by $\phi = 180 - \theta$ because the trans conformation ($\theta = 180^\circ$) has been selected as the energy origin. This fitting allows the analytical location of the singular points of the potential curve [32]. The reliability of this procedure has been tested in the most significant cases by means of a direct location of the critical points.

3. Results and discussion

STO-3G basis computations

The torsional potential energy curve obtained within the rigid rotor approximation is plotted in Fig. 2 (curve A). The cis conformation appears to be strongly unstabilized relative to the trans form, which is the absolute minimum of the curve. Against what was obtained in the 2,2'-bifuran system [24], the cis conformer corresponds to a maximum, and a shallow minimum appears at $\theta = 25.8^\circ$, $0.187 \text{ kcal mol}^{-1}$ lower in energy. The existence of the gauche minimum and the larger cis-trans stability difference obtained for 2,2'-bipyrrrole ($2.879 \text{ kcal mol}^{-1}$) relative to 2,2'-bifuran ($0.876 \text{ kcal mol}^{-1}$ at the same calculation level) [24] must be related to the appearance of sterical hindrance in the cis conformer of bipyrrrole due to the presence of the hydrogen atoms bound to the heteroatoms.

Partial optimization at STO-3G level was carried out as indicated above for 9 different conformations. The resulting potential energy curve is plotted in Fig. 2 (curve B) and the position and relative energies of critical points are summarized in Table 1. Cis and trans energies decrease 0.315 and $0.020 \text{ kcal mol}^{-1}$, respectively, relative to its rigid rotor values. Thus, interannular geometrical relaxation affects much more the cis conformer, where interannular nonbonded interactions are stronger, and, therefore, its unstabilization relative to the trans form decreases ($\Delta E_{\text{cis-trans}} = 2.584 \text{ kcal mol}^{-1}$). In the same way, the stability of the perpendicular conformation is affected by molecular relaxation and the trans \rightarrow gauche barrier reduces to $4.421 \text{ kcal mol}^{-1}$. The partially optimized curve B becomes very flat around the cis conformer and the gauche minimum almost disappears. This very shallow minimum, localized at $\theta = 19.2^\circ$, results only $0.049 \text{ kcal mol}^{-1}$ more stable than the cis disposition. If a full optimization of the geometry is carried out, it can be expected the minimum disappears as it occurs in systems with similar

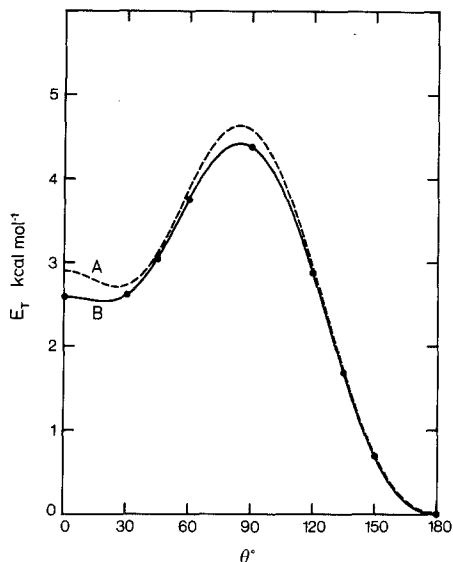


Fig. 2. Plots of the STO-3G total molecular energy, E_T , relative to the value for the trans partially optimized structure, as a function of the dihedral angle θ . *Curve A*: rigid rotor potential. Starting geometry and a 10° step in θ were used. *Curve B*: rotation potential after interannular parameters optimization. (See text for details)

H...H nonbonded interactions such as butadiene [29, 31] or vinylcyclopropane [33], for which a disappearance of the cisoid-gauche minimum after full optimization has been reported.

The coefficients V_i were obtained from the calculated total energies and are collected in Table 2. As it can be observed, the STO-3G rotational barrier is largely determined by V_2 and V_1 . The former reflects the tendency of the molecule to adopt a uniplanar conformation in order to maximize its conjugative stability, and the latter encompasses the effects of intramolecular dipole alignments, steric hindrance, and other nonbonded interactions. Since the remaining coefficients are small, V_1 is clearly the decisive factor in determining the relative stabilities

Table 1. Relative energies (ΔE , kcal mol $^{-1}$) and torsion angles ($^\circ$) for the critical points of the rotation potential of 2,2'-bipyrrrole. ΔE are relative to the computed trans conformer energy. The critical points are obtained from a n -term fitted Fourier expansion

	n	Trans (180°)		Transoid-gauche		Transition state		Cisoid-gauche		Cis (0°)
		E (hartree)	ΔE	θ	ΔE	θ	ΔE	θ	ΔE	
STO-3G ^a	6	-411.324275			4.614	84.1	2.692	25.8	2.879	
STO-3G _{p.o.} ^b	6	-411.324307			4.421	84.2	2.535	19.2	2.584	
4-31G/STO-3G _{p.o.} ^c	6	-415.867106	-0.458	147.7	1.813	84.0	1.143	46.3	2.742	
4-31G _{p.o.} ^b	4	-415.867685	-0.400	146.5	1.817	86.5	1.112	50.0	2.735	
	^d		-0.466	147.6	1.832	84.6	1.143	46.0		

^a Rigid rotor approach

^b Partial optimization involving the interannular region (see Fig. 1)

^c 4-31G calculations over partially optimized STO-3G structures

^d Direct location of critical points

Table 2. Coefficients (kcal mol⁻¹) of the truncated Fourier expansions

	V ₁	V ₂	V ₃	V ₄	V ₅	V ₆
STO-3G ^a	2.4543	3.2113	0.3190	-0.6140	0.1057	-0.0888
STO-3G _{p.o.} ^b	2.2917	3.1670	0.2500	-0.4863	0.0423	-0.0820
4-31G/STO-3G _{p.o.} ^c	2.3498	0.5193	0.3380	-1.1180	0.0542	-0.1193
4-31G _{p.o.} ^b	2.3461	0.4315	0.3889	-1.1283		

^{a,b,c} See Table 1 for details

of the cis and trans conformations. To be sure of the quality of the Fourier-fitted potential we have achieved direct optimization of the gauche minimum and it has been located at $\theta = 19.1^\circ$ and 2.528 kcal mol⁻¹ above the trans absolute minimum, in good agreement with the minimum calculated from the fitted potential $V(\phi)$ (see Table 1).

In general, and unlike what happens with biphenyl-like systems [34–37], our previous INDO calculations [22] correlates quite well with the STO-3G results reported here. Although the former does not predict any gauche minimum, the shape of the potential curves are both similar. The INDO cis-trans stability difference (0.795 kcal mol⁻¹) is smaller than the STO-3G one, while the trans \rightarrow cis potential barrier is very similar in both cases (INDO value is 5.080 kcal mol⁻¹). If one considers that the H1---H1' distance is notably shorter (2.08 Å) in the INDO cis-structure than in the STO-3G (2.25 Å) one, the cis-trans stability differences suggest that INDO method underestimates, with respect to STO-3G, the H1---H1' nonbonded interaction which plays a decisive role in determining the cis conformer stability.

Finally, STO-3G calculations on 2,2'-bipyrrrole have been very recently reported by Brédas et al. [38]. These authors only optimize the interannular bond and obtain a rotational barrier about 4 kcal mol⁻¹ and a cis-trans energy difference of 2.5 kcal mol⁻¹. Despite the differences in the limited optimization and the assumed ring geometries, our results are in good agreement with theirs.

4-31G basis computations

The 4-31G potential calculated over the partially optimized STO-3G structures (4-31G/STO-3G) is plotted in Fig. 3 (curve A). The critical points and relative energies obtained from the Fourier-fitted potential (Table 2) are reported in Table 1.

The shape of the torsional energy curve has changed drastically in comparison with the STO-3G curve. Now, we have a four-fold potential function. The 4-31G/STO-3G calculations locate the absolute minimum at a transoid-gauche position ($\theta = 147.7^\circ$) and the trans planar conformation at a maximum 0.458 kcal mol⁻¹ above it. The shallow cisoid-gauche minimum is also predicted but it appears to be deeper than in the STO-3G case and shifted to a greater value of the dihedral angle, $\theta = 46.3^\circ$. This second minimum lies 1.601 kcal mol⁻¹ above

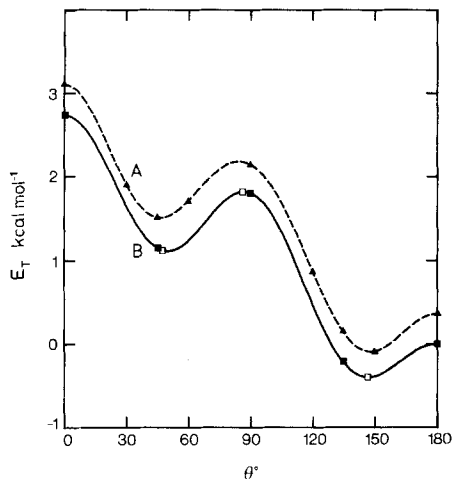


Fig. 3. Plots of the 4-31G total molecular energy, E_T , relative to the value for the trans partially optimized structure, as a function of the dihedral angle θ . *Curve A:* over partially optimized STO-3G geometries (4-31G/STO-3G). *Curve B:* after interannular parameters optimization. (\square) indicates the critical points after direct location of minima and a parabolic fitting in the surroundings of the transition state. (See text for details)

the transoid-gauche minimum and it is separated from the cis position by a barrier of $1.599 \text{ kcal mol}^{-1}$. The transition state between these minima lies at $\theta = 84.0^\circ$, it is $2.272 \text{ kcal mol}^{-1}$ above the transoid-gauche minimum, and it does not correspond to the most energetic conformation.

A limited geometrical optimization similar to that carried out at STO-3G level has been performed with 4-31G basis to test the influence of this basis change in the partial optimization. A four term truncated Fourier expansion was fitted to five optimized conformation energies and was used to get a first approach to the critical points. Then, a direct fitting in the surrounding of these critical points was performed. The results, summarized in Table 1 and Fig. 3 (curve B), show that the partial optimization with 4-31G basis set does not introduce significant changes in the shape of the curve and relative energies obtained from 4-31G/STO-3G calculations and the six terms Fourier fitting. The similar shape of both curves in Fig. 3 agrees with the statement by De Maré et al. [29, 39] that even the minimal basis set leads to geometries which can be used with larger basis sets to obtain reasonable relative conformational energies.

To summarize, an important destabilization of the cis and trans planar conformations relative to the perpendicular form, and consequent appearance of gauche minima, is observed when 4-31G is used instead of STO-3G. The reason for this destabilization might be searched in the H...H nonbonded interactions taking place in planar conformers and in the inadequacy of STO-3G basis set to account for them properly. Hence, as it occurs in the internal rotation around single bonds in conjugated systems, such as butadiene [29] and longer linear polyenes [40], some differences arise in the description of the conformational potential in going from STO-3G to the split valence basis. These differences are especially significant in the present case because they involve not only quantitative but strong qualitative differences in the shape of the potential, the most important of them being the prediction of the absolute maximum at cis conformation.

Structural parameters

The variation of the interannular bond length with θ is shown in Fig. 4. As it is well known, STO-3G overestimates the length of single bonds joining conjugated systems by 0.02–0.03 Å, while split valence calculations provide values very close to experiment [29, 41]. The X-ray diffraction value for d reported by J. M. André et al. [18] is 1.448 Å for the trans form, in complete agreement with our 4-31G distance (1.4476 Å). The very short length found in 2,2'-bipyrrrole for the interannular single bond in planar conformations at 4-31G level reveals a great delocalization between the two conjugated rings, and hence, a polyene-like behaviour. Indeed, this length d is even minor than that obtained at 6-31G level for the related polyenic system 1,3,5,7-octatetraene (1.4588 Å) [41]. Finally, the shortening in d at values of θ near 90°, when compared with the ethane single C—C bond length (1.523 Å), must be mainly attributed to hyperconjugative effects [42].

The two basis sets employed give very similar values for the bond angle α (see Fig. 1) in each conformation. So, α gets the values of 123.26 and 121.38° at STO-3G level and 123.35 and 121.64° at 4-31G level for cis and trans conformations, respectively. The X-ray diffraction value of α for the trans conformer is 121.5° [18]. The enlargement of this angle on going from trans to cis conformers can be seen as an attempt to diminish the steric hindrance and local dipole–dipole repulsion between the N1—H1 and N1'—H1' groups. In fact, these hydrogen atoms lie at 4-31G level only 2.22 Å apart in the cis conformer (the distance H3···H3' being longer, 2.60 Å), while in the trans form we have two symmetric H···H interactions at 2.41 Å. A further relaxation in the cis form of the planar angles concerning the N1—H1 and C3—H3 (and their counterparts) did not significantly change neither those H···H distances nor the relative energies.

The influence of the alignment of the local dipoles associated with N—H bonds in destabilizing the cis conformer cannot be ignored [43]. The resulting intramolecular dipole–dipole interaction would be a strongly basis dependent contribution to the total energy. Thus, the inclusion of polarization functions in the basis set would be desirable. However, extensive conformational studies

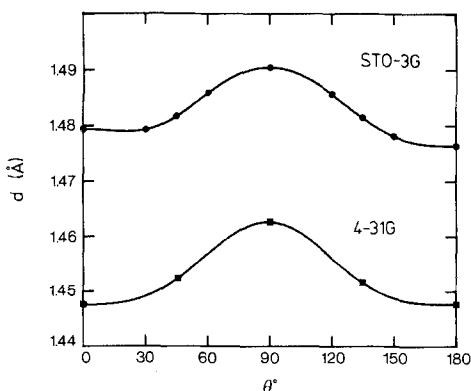


Fig. 4. Variation of the interannular distance, d , as a function of θ .

reported for smaller conjugated systems which include calculations with a number of different basis sets show that only small quantitative differences could be expected in relation to the 4-31G potential even with double polarized basis sets [29, 30, 44].

4. Conclusions

Ab initio calculations, using the 4-31G basis set, predict a four-fold torsional potential for 2,2'-bipyrrole. Two gauche minima occur in the vicinity of the planar conformations.

The description of the conformational behaviour of 2,2'-bipyrrole provided by STO-3G calculations is similar to that exhibited by linear polyenes for the rotation around a central single bond. However, two important features appear when split valence basis set is employed with 2,2'-bipyrrole: (i) the prediction of the cis conformer as the absolute maximum of the torsional potential and (ii) the appearance of a transoid-gauche minimum. Both differences can be directly related to the existence of repulsive nonbonded interactions at both sides of the interannular bond.

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References

1. Díaz, A. F., Kanazawa, K. K., Gardini, G. P.: *J. Chem. Soc., Chem. Commun.* 635 (1979)
2. Street, G. B., Clarke, T. C., Kroumbi, M., Kanazawa, K. K., Lee, V., Pfluger, P., Scott, J. C., Weiser, G.: *Mol. Cryst. Liq. Cryst.* **83**, 253 (1982)
3. Pfluger, P., Kroumbi, M., Street, G. B., Weiser, G.: *J. Chem. Phys.* **76**, 3212 (1983)
4. Scott, J. C., Pfluger, P., Kroumbi, M., Street, G. B.: *Phys. Rev. B* **28**, 2140 (1983)
5. Burgmayer, P., Murray, R. W.: *J. Phys. Chem.* **88**, 2515 (1984)
6. Skotheim, T. J., Lundström, I., Prejza, J.: *J. Electrochem. Soc.* **128**, 1625 (1981)
7. Skotheim, T. J., Peterson, L. G., Inghanas, O., Lundström, I.: *J. Electrochem. Soc.* **129**, 1737 (1982)
8. Bjorklund, R. B., Lundström, I.: *J. Electron. Mater.* **13**, 211 (1984)
9. Díaz, A. F., Vallejo, J. M., Duran, A. M.: *IBM J. Res. Dev.* **25**, 42 (1981)
10. Yakushi, K., Lauchian, L. J., Clarke, T. C., Street, G. B.: *J. Chem. Phys.* **79**, 4774 (1983)
11. Salaneck, W. R., Erlandsson, R., Prejza, J., Lundström, I., Inghanas, O.: *Synth. Met.* **5**, 125 (1983)
12. Pfluger, P., Street, G. B.: *J. Chem. Phys.* **80**, 544 (1984)
13. Ford, W. K., Duke, C. B., Salaneck, W. R.: *J. Chem. Phys.* **77**, 5030 (1982)
14. Brédas, J. L., Thémans, B., André, J. M.: *J. Chem. Phys.* **78**, 6137 (1983)
15. Brédas, J. L., Silbey, R., Boudreaux, D. S., Chance, R. R.: *J. Am. Chem. Soc.* **105**, 6555 (1983)
16. Brédas, J. L., Thémans, B., Fripiat, J. G., André, J. M., Chance, R. R.: *Phys. Rev. B* **29**, 6761 (1984)
17. Brédas, J. L., Scott, J. C., Yakushi, K., Street, G. B.: *Phys. Rev. B* **30**, 1023 (1984)
18. André, J. M., Vercauteren, D. P., Street, G. B., Brédas, J. L.: *J. Chem. Phys.* **80**, 5643 (1984)
19. Welsh, W. J., Jaffé, H. H., Kondo, N., Mark, J. E.: *Makromol. Chem.* **183**, 801 (1982)
20. Shank, C. V., Yen, R., Fork, R. L., Orenstein, J., Baker, G. L.: *Phys. Rev. Lett.* **49**, 1660 (1982)
21. Galasso, V., Trinajstić, N.: *Tetrahedron* **28**, 4419 (1972)
22. Ortí, E., Tomás, F., Sánchez-Marín, J.: *J. Mol. Struct., Theochem* **104**, 197 (1983)

23. Nygaard, L., Nielsen, J. J., Kirchheiner, J., Maltesen, G., Rastrup-Andersen, J., Sorensen, G. O.: *J. Mol. Struct.* **3**, 491 (1969)
24. Ortí, E., Sánchez-Marín, J., Tomás, F.: *J. Mol. Struct., Theochem* **108**, 199 (1984)
25. Hehre, W. J., Lathan, W. A., Ditchfield, R., Newton, M. D., Pople, J. A.: GAUSSIAN-70, QCPE Program No. 236 (1973)
26. Hehre, W. J., Stewart, R. F., Pople, J. A.: *J. Chem. Phys.* **51**, 2657 (1969)
27. Ditchfield, R., Hehre, W. J., Pople, J. A.: *J. Chem. Phys.* **54**, 724 (1971)
28. Payne, P. W., Allen, L. C.: Barriers to rotation and inversion. In: Schaefer III, H. F., (ed.) *Applications of electronic structure theory*, Chap. 2. New York: Plenum Press 1977
29. De Maré, G. R., Neisius, D.: *J. Mol. Struct., Theochem* **109**, 103 (1984)
30. Bock, C. W., George, P., Trachtman, M.: *Theoret. Chim. Acta (Berl.)* **64**, 293 (1984)
31. De Maré, G. R.: In: Csizmadia, I. G., Daudel, R. (eds.) *Computational theoretical organic chemistry*. NATO ASI Ser. C **67**, 371 (1981)
32. Radom, L., Hehre, W. J., Pople, J. A.: *J. Am. Chem. Soc.* **94**, 2371 (1972)
33. De Maré, G. R., Peterson, M. R.: *J. Mol. Struct., Theochem* **89**, 213 (1982)
34. Scharfenberg, P., Jung, C.: *Chem. Phys. Lett.* **57**, 131 (1978)
35. Birner, P., Hofmann, H.-J.: *Int. J. Quantum Chem.* **21**, 833 (1982)
36. Momicchioli, F., Baraldi, I., Bruni, M. C.: *Chem. Phys.* **70**, 161 (1982)
37. Barone, V., Lelj, F., Cauletti, C., Piancastelli, M. N., Russo, N.: *Mol. Phys.* **49**, 599 (1983)
38. Brédas, J. L., Street, G. B., Thémans, B., André, J. M.: *J. Chem. Phys.* **83**, 1323 (1985)
39. De Maré, G. R., Peterson, M. R.: *J. Mol. Struct., Theochem* **104**, 115 (1983)
40. Rao, B. K., Darsey, J. A., Kestner, N. R.: *J. Chem. Phys.* **79**, 1377 (1983)
41. Bock, C. W., George, P., Trachtman, M.: *J. Mol. Struct., Theochem* **109**, 1 (1984)
42. Daudey, J. P., Trinquier, G., Barthelat, J. C., Malrieu, J. P.: *Tetrahedron* **36**, 3399 (1980)
43. Charge distributions are available upon request from the authors. 4-31G total dipole moments for the transoid- and cisoid-gauche minima are 0.95 and 2.90 D respectively
44. Osamura, Y., Schaefer III, H. F.: *J. Chem. Phys.* **74**, 4576 (1981); De Maré, G. R.: *J. Mol. Struct., Theochem* **107**, 127 (1984)