Cross-Conjugation: A Theoretical and Experimental Study of the Molecular Structure of 2-Ethynyl-1,3-butadiene [‡]

M. Trætteberg[†,a] and H. Hopf[b]

[a]Department of Chemistry, University of Trondheim, AVH, N-7055 Dragvoll, Norway and [b]Institute of Organic Chemistry, University of Braunschweig, Hagenring 30, D-38106 Braunschweig, Germany

Trætteberg, M. and Hopf, H., 1994. Cross-conjugation: A Theoretical and Experimental Study of the Molecular Structure of 2-Ethynyl-1,3-butadiene. – Acta Chem. Scand. 48: 989–993 © Acta Chemica Scandinavica 1994.

The molecular structure of the cross-conjugated compound 2-ethynyl-1,3-butadiene has been studied experimentally using the gas-phase electron diffraction method, and theoretically by ab initio HF and MP2 calculations, using the 6-31G* basis set. The molecule was found to have a planar anti conformation. The cross-conjugated C = C bond was observed to be ca. 0.01 Å longer than the other C = C bond, in agreement with the C = C bond differences calculated in the theoretical studies. The agreement between the observed and calculated molecular geometry is generally excellent.

Cross-conjugation is a phenomenon that has been much less widely studied than through-conjugation, even though cross-conjugated compounds are not uncommon in organic chemistry. Examples are found in quinones, fulvenes, radialenes,[1] many dyestuffs, fused-ring aromatics, as well as in cross-conjugated polymers (dendralenes).[2]

Among the cross-conjugated hydrocarbons 3-methylene-1,4-pentadiene (2-vinyl-1,3-butadiene) and 3-methylene-penta-1-en-4-yne (2-ethynyl-1,3-butadiene) are the simplest ones. The former compound was thoroughly investigated a few years ago by gas-phase electron diffraction, as well as by vibrational, NMR and ultraviolet spectroscopy.[3] The cross-conjugated bond in this molecule was observed to be slightly longer than the other CC double bonds. The GED data revealed the presence of only an anti,skew conformation, consisting of an anti 1,3-butadiene fragment, with the vinyl substituent in 2-position having a 40° dihedral angle, relative to a local s-cis conformation (0°). When the two π-systems of 1,3-butadienyl and vinyl are connected to a cross-conjugated molecule, the preferable arrangement of the combined π-system would be compatible with a coplanar molecule. In principle there are three possible planar conformations of 2-vinyl-1,3-butadiene (anti,anti, anti,syn and syn,syn). All of these do, however, give rise to substantial non-bonded repulsions, and the observed anti,skew conformation appears to be the result of a compromise between favour-able π-electron interactions and unfavourable van der Waals forces.

When a 1,3-butadienyl and an ethynyl π-system are connected to form a cross-conjugate molecule the only possible coplanar π-system arrangements are those that might exist in 1,3-butadiene (anti or syn). As substitution of an ethynyl group in the 2-position of the energetically favoured anti 1,3-butadiene conformer is not expected to give rise to severe non-bonded repulsion, the 2-ethynyl-1,3-butadiene molecule is expected to retain a planar anti minimum-energy conformation. The vibrational spectra of 2-ethynyl-1,3-butadiene in the vapour, liquid and crystalline state were recently studied by Priebe et al.[4] Their data indicated that the molecule exists as a s-trans (anti) conformer in all three aggregation states, although the possibility of small amounts of a second conformer could not be excluded.

The present study is aimed at determining the geometry of the 2-ethynyl-1,3-butadiene molecule with highest possible precission, using experimental as well as theoretical methods.

Electron diffraction structure study

Experimental. The title compound was prepared by pyrolysis of 1,2-hexadien-5-yne in a flow reactor at 770 K.[5] An analytically pure sample was obtained from the pyrosylate by preparative gas chromatography (Carbowax, 60°C). Electron diffraction diagrams were recorded with the Oslo apparatus[6] using a nozzle-tip temperature of 293 K. The electron wavelength was 0.064 66 Å, as calibrated against the diffraction pattern of benzene. The estimated uncertainty in the determination of the wave-
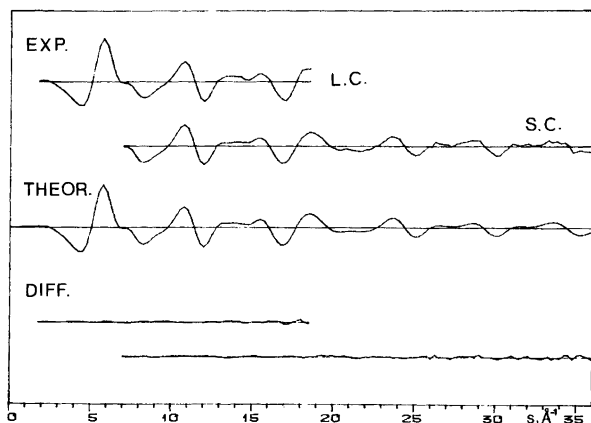
Fig. 1. Experimental and theoretical molecular intensities for 2-ethynyl-1,3-butadiene and the difference curves. L.C.: Long camera data; S.C.: short camera data. The theoretical curve is calculated from the parameters in Tables 1 and 2.

length is 0.1%. Electron diffraction photographs were recorded on Kodak Electron Image plates at nozzle-to-plate distances of 485.13 mm (6 plates) and 205.13 mm (6 plates). The scattering ranges of the data were 1.50–18.75 and 7.00–43.25 Å^{-1}, with Δs increments of 0.25 Å^{-1}. The intensity data beyond $s = 36.00$ Å^{-1} were not used because of their low signal-to-noise ratio. The experimental data were treated in the usual way,[7] and the modification function used was $s \cdot f_C^{-2}$. The scattering amplitudes and phases were calculated[8] using the partial-wave method, based upon the analytical HF potentials for the C atoms[9] and the best electron density of bonded hydrogen for the H atoms.[10] The inelastic scattering fac-

tors used were those of Tavard *et al.*[11] The experimental molecular intensity curve is presented in Fig. 1.

Structure determination. The molecular structure of 2-ethynyl-1,3-butadiene was studied by interactive least-squares intensity refinements. The non-bonded interatomic distances of the molecular model were calculated on the basis of r_α parameters, which include corrections for shrinkage effects.[12]

Normal coordinate calculations were carried out for a molecular model of 2-ethynyl-1,3-butadiene, yielding the vibrational amplitudes (u_{ij}) for all interatomic distances, as well as the perpendicular correction coefficients (K_{ij}) necessary for carrying out a GED study, including shrinkage corrections. The normal coordinate analysis was based on the quantum-mechanical force field for 1,3-butadiene.[13] The calculated vibrational frequencies were generally in good agreement with those observed.[4]

Even though 2-ethynyl-1,3-butadiene is a small molecule, a large number of parameters is necessary to define its geometry. All CC bond lengths are, for example, expected to be unequal. In the present study the molecular model was defined by 14 geometric parameters, comprising five different CC bonds $(C^1 = C^2,\ C^3 = C^4,\ C^2-C^3,\ C^2-C^5,\ C \equiv C)$, two CH bonds $(C^2_{sp}-H$ and $C_{sp}-H)$, three $C = C-C$ angles $(C^1 = C^2-C^3,\ C^2-C^3 = C^4$ and $C^1 = C^2-C^5)$, three $C = C-H$ angles [terminal $C = C-H$ (except for $C^3 = C^4-H^{11}$), $C^3 = C^4-H^{11}$ and $C^4 = C^3-H^9$] and the $C^1 = C^2-C^3 = C^4$ dihedral angle. Inherent in this model are the assumptions of equal $C_{sp^2}-H$ bond lengths, of linearity of the $C-C \equiv C-H$ fragment and of equality of the terminal $C = C-H$ valence angles, with the exception

Table 1. 2-Ethylnyl-1,3-butadiene: geometric parameters obtained from GED least-squares intensity refinements and from theoretical calculations.[a]

| | GED | | HF/6-31G* | MP2/6-31G* | VBD (GED) |
	R_a	R_α			R_a
Bonds					
$C^1 = C^2$	1.357(8)	1.350	1.328	1.352	1.349(18)
$C^3 = C^4$	1.342(10)	1.320	1.321	1.342	1.342(10)
$C^5 \equiv C^6$	1.215(3)	1.206	1.188	1.223	
C^2-C^3	1.418(3)	1.475	1.478	1.470	1.479(3)
C^2-C^5	1.433(4)	1.431	1.447	1.436	
$C_{sp}-H$	1.062(72)	1.032	1.057	1.067	
$C_{sp^2}-H$	1.091(16)	1.073	1.075	1.086	1.091(3)
Bond angles					
$C^1 = C^2-C^3$	122.0(7)		121.4	121.4	121.7(1.4)
$C^2-C^3 = C^4$	126.0(1.0)		125.7	124.6	125.2(6)
$C^1 = C^2-C^5$	120.0(1.1)		120.0	120.2	118.7(2.7)
$C = C-H$	123.0(1.0)[b]		121.5[b]	121.3[b]	
$C^4 = C^3-H^9$	120.0[c]		119.7	120.0	
Dihedral angle					
$C^1 = C^2-C^3 = C^4$	180.0[c]		180.0[c]	180.0[c]	

[a] Distances are in Å, angles are in ° and 2σ values are in parentheses. Relevant parameters determined for 2-vinyl-1,3-butadiene (VBD)[3] are shown for comparison. [b] The terminal $C = C-H$ angles are assumed to be equal. [c] Fixed.

Table 2. 2-Ethynyl-1,3-butadiene: calculated and observed vibrational amplitudes and the standard deviations.[a]

$R_a/Å$[b]	$u_{obs}/Å$		$u_{calc}/Å$	$R_a/Å$	$u_{obs}/Å$		$u_{calc}/Å$
$C^1=C^2$ (1.357)	0.039		0.042	$C^5 ·· H^7$ (2.69)	0.082		0.096
$C^3=C^4$ (1.342)	0.039		0.042	$C^5 ·· H^{11}$ (2.77)	0.165		0.180
$C≡C$ (1.215)	0.033	(2)	0.036	$C^1 ·· H^9$ (2.66)	0.120	(20)	0.135
C^2-C^3 (1.481)	0.045		0.048	$C^3 ·· H^8$ (2.76)	0.082		0.097
C^2-C^5 (1.433)	0.043		0.046	$C^2 ·· H^{11}$ (2.89)	0.121		0.136
$C^1 · C^5$ (2.41)	0.060		0.061	$C^5 ·· H^8$ (3.41)	0.195		0.135
$C^1 · C^3$ (2.48)	0.059		0.061	$C^3 ·· H^7$ (3.47)	0.195		0.135
$C^2 · C^4$ (2.50)	0.060	(2)	0.062	$C^6 ·· H^7$ (3.55)	0.163	(31)	0.103
$C^3 · C^5$ (2.50)	0.063		0.065	$C^2 ·· H^{10}$ (3.48)	0.158		0.098
$C^2 · C^6$ (2.64)	0.049		0.050	$C^5 ·· H^9$ (3.42)	0.161		0.100
$C^4 ·· C^5$ (2.93)	0.085	(6)	0.104	$C^2 ·· H^{12}$ (3.68)	0.146		0.086
$C^1 ·· C^6$ (3.51)	0.081		0.078	$C^5 ··· H^{10}$ (4.01)	0.115		0.126
$C^3 ·· C^6$ (3.58)	0.086		0.083	$C^4 ··· H^8$ (4.06)	0.096	(23)	0.106
$C^1 ·· C^4$ (3.70)	0.066	(4)	0.063	$C^1 ··· H^{11}$ (4.20)	0.123		0.134
$C^4 ·· C^6$ (3.71)	0.149		0.146	$C^1 ··· H^{12}$ (4.50)	0.111		0.120
C^6-H (1.06)	0.072		0.074	$C^6 ··· H^8$ (4.56)	0.156		0.165
C^1-H (1.09)	0.075	(4)	0.077	$C^1 ··· H^{10}$ (4.58)	0.100		0.109
C^3-H (1.09)	0.075		0.077	$C^4 ··· H^7$ (4.62)	0.127	(13)	0.135
$C^4 · H^9$ (2.12)	0.101		0.098	$C^4 ···· H^{12}$ (4.53)	0.199		0.207
$C^3 · H^{10}$ (2.13)	0.101		0.098	$C^3 ··· H^{12}$ (4.56)	0.117		0.126
$C^2 · H^7$ (2.15)	0.101	(7)	0.098	$C^6 ··· H^9$ (4.57)	0.097		0.106
$C^2 · H^8$ (2.15)	0.101		0.098	$C^6 ···· H^{10}$ (4.75)	0.165		0.174
$C^3 · H^{11}$ (2.21)	0.101		0.098	$C^6 ···· H^{11}$ (3.20)	(0.221)		0.221
$C^2 · H^9$ (2.17)	0.105		0.102				
$C^5 · H^{12}$ (2.26)	0.082		0.079				

[a] The interatomic distances are given in parentheses. [b] The number of dots indicates the number of bond angles separating the atoms.

of that involving the sterically somewhat strained H^{11} atom. The assumption about the equality of the three terminal C = C–H valence angles is supported by results obtained from ab initio calculations, in which these angles were found to be nearly equal.

It was not possible to detect any sign of deviation from the planarity of the molecule, and in order to reduce the
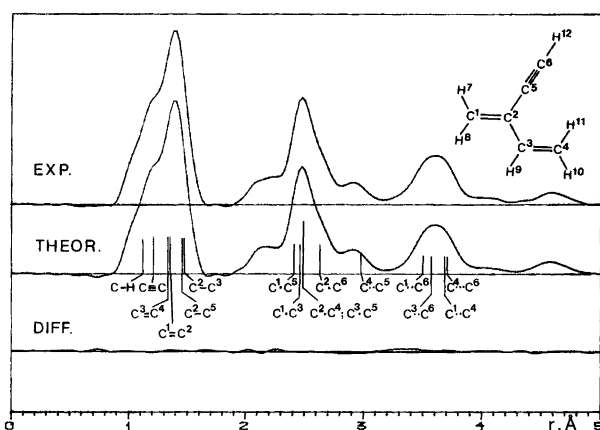

Fig. 2. Experimental and theoretical radial distribution curves for 2-ethynyl-1,3-butadiene. The theoretical curve is calculated from the parameters given in Tables 1 and 2. The numbering of the atoms that has been applied is illustrated. The vertical bars indicate the positions of the various non-bonded CC distances.

number of parameters the $C^1 = C^2-C^3 = C^4$ dihedral angle was fixed at 180° in the final refinements. It was further necessary to exclude the $C^4 = C^3-H^9$ angle from the refinement scheme, as reliable results could not be obtained for this parameter.

Table 1 shows the final structural results obtained from the GED study of 2-ethynyl-1,3-butadiene. In this model all geometric parameters, except $\angle C^4 = C^3-H^9$ and the $C^1 = C^2-C^3 = C^4$ torsion angle, have been refined, as well as most of the vibrational amplitudes (in groups). The results obtained for the latter are presented in Table 2, where the corresponding data resulting from the normal coordinate calculation are also included. The theoretical intensity curve calculated from the parameters given in Tables 1 and 2 is shown in Fig. 1, together with the experimental intensity curves, while the corresponding theoretical and experimental radial distribution curves are presented in Fig. 2.

Theoretical structure study

The theoretical ab initio calculations were carried out using the program GAUSSIAN92.[14] They include HF[15] as well as MP2[16] calculations, using the 6-31G* basis set, and including complete geometry optimization. The calculations were performed on a CRAY Y-MP at SINTEF/NTH in Trondheim. The results from the calculations are presented in Table 1.

Discussion

The electron diffraction study shows that the 2-ethynyl-1,3-butadiene molecule exists in a planar *anti* equilibrium conformation in the vapour phase, in contrast to the structurally related cross-conjugated molecule 2-vinyl-1,3-butadiene, which has a *gauche* or *skew* oriented 2-vinyl group ($\theta(C^1 = C^2-C^5 = C^6)$: 39°) and a planar *anti* 1,3-butadiene skeleton.[3] This is, however, hardly surprising, as the internal nonbonded repulsions between the cross-conjugation unsaturated groups of a coplanar *anti,anti* conformation of 2-vinyl-1,3-butadiene would be substantially larger than is the case for 2-ethynyl-1,3-butadiene. However, non-bonded repulsion between the cross-conjugating groups is to some extent also present in 2-ethynyl-1,3-butadiene and influences the structure parameters of the molecule. Table 3 shows the geometrical parameters for 2-ethynyl-1,3-butadiene and for the two fragment molecules, 1,3-butadiene and 1-buten-3-yne, as obtained by *ab initio* MP2 calculations, using 6-31G* basis sets. Experimental GED results for the three molecules are given in parentheses. Compared to the (equal) C = C–C angles in 1,3-butadiene, the $C^1 = C^2-C^3$ angle in 2-ethynyl-1,3-butadiene is decreased by 2.3°, while the $C^2-C^3 = C^4$ angle is increased by 0.9°. Both these modifications have the effect of increasing the distances between the atoms of the two cross-conjugating groups. When the 1-buten-3-yne skeleton is compared with the similar fragment in 2-ethynyl-1,3-butadiene the same effect is observed, as the $C^1 = C^2-C^5$ angle is reduced by 3.1° in the latter molecule.

Theoretical studies[17-21] of bond orders in cross-conjugated hydrocarbon systems indicate that the π-electron distribution in cross-conjugated polyenes differ systematically from those in linear polyenes. The main effect of cross-conjugation should be one of π-bond delocalization in the direction through the C = C double bond. In the present case the experimental as well as the theoretical structural results are in agreement with this description, as the cross-conjugated $C^1 = C^2$ bond is found to be

0.010–0.015 Å longer than the other C = C bond. The observed difference between the crossconjugated $C^1 = C^2$ and the other C = C bond length is larger in 2-ethynyl-1,3-butadiene (0.015 Å) than in 2-vinyl-1,3-butadiene (0.007 Å), where the *skew,anti* conformation prevents an optimal interaction of the π-orbitals. The observed distributions of CC distances in the two molecules are therefore reasonable and in agreement with current theories of the effect of π-electron crossconjugation. It should, however,be noted that when the error limits of the observed C = C bond lengths are taken into account, the observed bond length differences support the theoretical descriptions of crossconjugated hydrocarbons, but they can hardly be used as proofs.

From Table 1 it might be seen that the R_a-R_x CC bond differences obtained for 2-ethynyl-1,3-butadiene are smaller then 0.010 Å, except for $C^3 = C^4$, where this difference is 0.022 Å. R_x represents the distance between average atomic coordinates, and a large R_a-R_x difference may therefore indicate that relatively extense internal rotations or vibrations are taking place. In the present case the R-values obtained for the $C^3 = C^4$ bond may be interpreted as a result of oscillations of the relatively light-weight vinyl group to both sides of the plane of the equilibrium conformation.

It is of interest to compare the structural parameters determined for 2-ethynyl-1,3-butadiene with those of its building blocks: 1,3-butadiene[22] and 1-buten-3-yne.[23] Both molecules have been studied by GED[22,23] and we have additionally carried out theoretical *ab initio* MP2/6-31G* calculations with full geometry optimization for 2-ethynyl-1,3-butadiene as well as for its two fragment molecules. The theoretical and experimental data for the three molecules are presented in Table 3. The agreement between the experimental and theoretical results is generally very satisfactory.

The lengthening effect due to crossconjugation has been commented on above, and the observed and calculated differences between the $C^1 = C^2$ bond lengths in 2-ethynyl-1,3-butadiene and 1,3-butadiene are equal

Table 3. Structural parameters (distances in Å, angles in °) obtained by *ab initio* MP2/6-31G* calculations and by experimental GED studies (in parentheses) for 2-ethynyl-1,3-butadiene and its building fragments, 1,3-butadiene[22] and 1-buten-3-yne[23].

$r(C^1=C^2)$	1.352 (1.357)	1.344 (1.349)	1.344 (1.341)
$r(C^3=C^4)$	1.342 (1.342)	1.344 (1.349)	
$r(C^2-C^3)$	1.470 (1.481)	1.458 (1.467)	
$r(C^2-C^5)$	1.436 (1.433)		1.430 (1.431)
$r(C\equiv C)$	1.223 (1.215)		1.223 (1.209)
$\angle C^1=C^2-C^3$	121.4 (122.0)	123.7 (124.4)	
$\angle C^2-C^3=C^4$	124.6 (126.0)	123.7 (124.4)	
$\angle C^1=C^2-C^5$	120.2 (120.0)		123.3 (123.0)
E(MP2/6-31G*)	−233.763 1432	−155.422 6363	−154.205 5804

(0.008 Å). The C^2–C^3 bond in 2-ethynyl-1,3-butadiene is observed to be 0.014 Å longer than in 1,3-butadiene, in good agreement with the calculated bond differences (0.012 Å). A smaller bond length difference (0.006 Å) is calculated for the C^2_{sp}–C_{sp} bonds in 2-ethynyl-1,3-butadiene and 1-buten-3-yne, while the corresponding experimental bonds were nearly equal ($\Delta = 0.002$ Å). The error limits of the experimental data do not justify a discussion of the significance of experimental bond distance differences of the order of 10^{-3} Å, but it is gratifying that the observed variation in the C^2_{sp}–C_{sp} bonds are in general agreement with the results from the theoretical calculations.

The calculated C^2–C^3 and C^2–C^5 single bonds in 2-ethynyl-1,3-butadiene are found to be slightly larger than in the fragment molecules 1,3-butadiene and 1-buten-3-yne. The effect from cross-conjugation through the CC single bond is expected to be very small, but should eventually result in π-electron localization and a slightly smaller C–C bond, in contrast to what is found in this study. A possible explanation of the calculated lengthening of the C^2–C^3 and C^2–C^5 bonds, relative to those in the two reference molecules, could be connected to the differences in C = C–C valence angles, as discussed above. In 2-ethynyl-1,3-butadiene both relevant C = C–C angles are smaller than in the fragment molecules, corresponding to a reduced s-character in the substituent hybrid orbitals used in the formation of the C–C bonds. This is, however, not a very convincing argument, as the bond lengthening is calculated to be larger for the C^2–C^3 than for the C^2–C^5 bond, whereas the C^3 hybrid orbital in 2-ethynyl-1,3-butadiene according to the same argumentation should have slightly increased s-character, owing to a small increase (0.9°) in $\angle C^2$–C^3 = C^4. Theoretical *ab initio* MP2/6-31G* geometry optimizations of the molecules 1,3-butadiene, 2-methyl-1,3-butadiene and 2,3-dimethyl-1,3-butadiene give C^2–C^3 bonds of 1.458, 1.467 and 1.478 Å. The C^2–C^3 and C^2–C^5 bond lengths discussed above for 2-ethynyl-1,3-butadiene are therefore probably primarily a result of substitution and not of crossconjugation.

References

1. Hopf, H. and Maas, G. *Angew. Chem., Int. Ed. Engl. 31* (1992) 931.
2. Hopf, H. *Angew. Chem., Int. Ed. Engl. 23* (1984) 948.
3. Almenningen, A., Gatial, A., Grace, D. S. B., Hopf, H., Klæboe, P., Lehrich, F., Nielsen, C. J., Powell, D. L. and Trætteberg, M. *Acta Chem. Scand., Ser. A 42* (1988) 634.
4. Priebe, H., Nielsen, C. J. and Klæboe, P. *J. Mol. Struct. 158* (1987) 249.
5. Hopf, H. *Chem. Ber. 104* (1971) 1499.
6. Bastiansen, O., Hassel, O. and Risberg, F. *Acta Chem. Scand. 9* (1955) 232.
7. Hagen, K. and Hedberg, K. *J. Chem. Phys. 51* (1969) 2500.
8. Yates, A. C. *Comput. Phys. Commun. 2* (1971) 175.
9. Strand, T. G. and Bonham, R. A. *J. Chem. Phys. 40* (1964) 1686.
10. Stewart, R. F., Davidson, E. R. and Simpson, W. T. *J. Chem. Phys. 42* (1965) 3175.
11. Tavard, C., Nicolas, D. and Rouault, M. *J. Chim. Phys. 64* (1967) 540.
12. Kuchitsu, K. and Cyvin, S. J. In: Cyvin, S. J., Ed., *Molecular Structures and Vibrations*, Elsevier, Amsterdam 1972, Chap. 12.
13. Pulay, P., Fogarasi, G., Pongor, G., Boggs, J. E. and Vargha, A. *J. Am. Chem. Soc. 105* (1983) 7037.
14. Gaussian 92, Revision A, Frisch, M. J., Trucks, G. W., Head-Gordon, M., Gill, P. M. W., Wong, M. W., Foresman, J. B., Johnson, B. G., Schlegel, H. B., Robb, M. A., Replogle, E. S., Gomperts, R., Andres, J. L., Raghavachari, K., Binkley, J. S., Gonzales, C., Martin, R. L., Fox, D. J., Defrees, D. J., Baker, J., Stewart, J. J. P. and Pople, J. A., Gaussian, Inc., Pittsburgh PA 1992.
15. Roothan, C. C. J. *Rev. Mod. Phys. 23* (1951) 69.
16. Møller, C. and Plesset, M. S. *Phys. Rev. 46* (1934) 618.
17. Streitweiter, A., Jr. *Molecular Orbital Theory for Organic Chemists*, Wiley, New York 1966, pp. 59–61.
18. Phelan, N. F. and Orchin, M. *J. Chem. Educ. 45* (1968) 633.
19. Heilbronner, E. and Bock, H. *The HMO Model and its Applications*, Wiley, New York 1967, p. 47.
20. Banks, A., Mains, G. J., Bock, C. W., Trachtman, M. and George, P. *J. Mol. Struct. 56* (1979) 267.
21. Janssen, J. and Lüttke, W. *J. Mol. Struct. 81* (1982) 73.
22. Kveseth, K., Seip, R. and Kohl, D. A. *Acta Chem. Scand., Ser. A 34* (1980) 31.
23. Fukuyama, T., Kuchitsu, K. and Morino, Y. *Bull. Chem. Soc. Jpn. 42* (1969) 379.