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The molecular structure of 1,1-dicyanocyclopentane from gas electron diffraction data and ab initio calculations[☆]

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Abstract

The molecular structure of 1,1-dicyanocyclopentane (DCCP) has been investigated by means of gas-phase electron diffraction and ab initio calculation. Although the electron diffraction data could be fairly good reproduced by a C_s (envelope) model we found it more pertinent to apply a pseudorotation model to account for the dynamic and large amplitude motion in DCCP. Based on this model we analyzed the dependency of the ring geometric parameters and vibrational mean amplitudes on the phase angle ϕ . For a better elucidation of this distinct dependency we developed particular equations which describe the dependency of the distribution of the delocalized net charges throughout the ring on the phase angle ϕ .

For the purpose of a more systematical study of the substituent effect exerted by the cyano group we also investigated the structure and conformational stability of monocyanocyclopentane (MCCP) by means of various quantum mechanical methods. The MP2 method in combination with the basis sets 6-311 + G(2df,2pd), 6-311 + G(d,p), and 6-31G(d,p) favors the *axial* conformer which is in contradiction to earlier results which were obtained from electron diffraction data [J. Mol. Struct., 116 (1984) 29]. Using the same basis sets but the DFT/B3PW91 method, however, leads to a more stable *equatorial* conformer. This striking behavior is discussed in this paper.

The joint electron diffraction and ab initio study has led to the following r_α structural parameters of DCCP: $r(\text{C}\equiv\text{N}) = 1.152(2)$ Å, $r(\text{C}-\text{C}\equiv) = 1.472(5)$ Å, average $r(\text{C}-\text{C})_{\text{ring}} = 1.549(3)$ Å, $\angle(\text{C}_5-\text{C}_1-\text{C}_2) = 103.6(26)^\circ$, $\angle(\text{NC}-\text{C}-\text{CN}) = 109.0(35)^\circ$, $\angle(\text{C}-\text{C}\equiv\text{N}) = 175.2(33)^\circ$, and $\angle(\text{H}-\text{C}-\text{H}) = 112.7(23)^\circ$. The puckering amplitude for the five-membered ring was determined to be $q = 0.434(45)$ Å.

The quantum mechanical calculations were carried out by utilizing the Hartree–Fock, density functional B3PW91, and perturbation MP2 methods and applying the basis sets: 6-31G(d,p), 6-311G(df,pd), 6-311 + G(d,p) and 6-311 + (2df,2pd).

In contrast to the Mulliken population analysis the natural population analysis provided clear evidence for the electronic interaction and bond conjugation within the geminally substituted cyano groups. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: 1,1-Dicyanocyclopentane; Monocyanocyclopentane; Pseudorotation; Non-linearity and conjugation of geminal cyano groups; Charge distribution and natural population analysis versus Mulliken population analysis

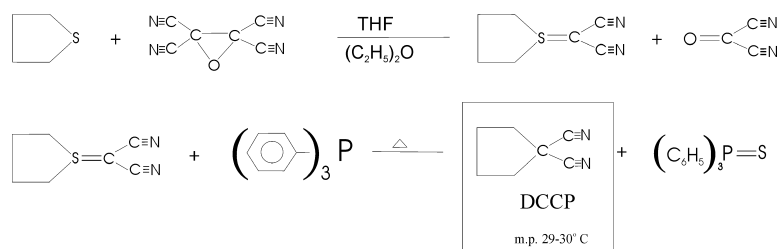
[☆] “This paper is dedicated to Professor Paolo G. Favero and Professor Helmut Dreizler in appreciation of their significant contributions to the field of microwave spectroscopy”.

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1. Introduction

As a continuation of our efforts to contribute to a better understanding of the effects of substituents on the geometry and dynamics of cyclic systems we



Scheme 1.

investigated the structure of 1,1-dicyanocyclopentane (DCCP) by means of electron diffraction and ab initio calculations. Static (rigid) one-conformer (for each the C_s and C_2 forms) and two conformers (C_s plus C_2) model as well as a model considering the pseudorotational motion have been used to fit the experimental data.

Major reasons for initiating the present study are: (1) To obtain additional pertinent results which may contribute to a more complete and perhaps detailed understanding of the pseudorotational motion in five-membered rings. (2) To explore the influence of the geminal cyano groups on the pseudorotational parameters of the five-membered ring, the phase angle ϕ and the puckering amplitude q . (3) To extend our earlier investigations of the reasons leading to the non-linearity of geminally substituted cyano groups and whether this structural peculiarity is the result of direct conjugation and/or steric interaction. (4) To elucidate the role of the electrophilic cyano group by the stabilization of the envelope (C_s) or half-chair (C_2) conformation.

It has been long recognized that the potential function for the hindered pseudorotation in substituted cyclopentanes depends substantially on the charge affinity of the substituent and the kind of electronic interaction with the ring system. In this context DCCP with its cyano groups as strong π - and σ -electron acceptors in geminal arrangement represents undoubtedly a unique testing example in this respect.

2. Synthesis and experimental data

According to the scheme shown above the reaction between tetrahydrothiophane and tetracyanoethylene epoxide provided the corresponding sulfoniumdicyanomethylide. The subsequent transylation of triphenylphosphine with the ylide gave DCCP [1] (Scheme 1).

Recordings of the diffraction patterns at two camera distances were obtained with the apparatus of the Hungarian diffraction group in Budapest. Two sets of data were obtained at approximate camera distances of 19 and 50 cm. The experimental conditions are summarized in Table 1, and the intensity data are deposited as supplementary material. Our usual data reduction and refinement procedures were used [2,3], and the atomic scattering amplitudes and phases of Haase [4] were applied.

3. Ab initio calculations

The ab initio computations were carried out on various levels of theory using the programs GAUSSIAN 98 [5] and SPARTAN [6]. The following methods were applied: HF/6-31G**, B3PW91/6-311++G(df,pd), B3PW91/6-31G*, B3PW91/6-311+G(2df,2pd), MP2/6-31G**, and MP2/6-311+G(2df,2pd). All these methods, particularly the perturbation methods, provided results which are in good agreement with the experiment.

Table 1
Experimental conditions of the diffraction experiment

Camera distance (mm)	Temperature nozzle (°C)	Wavelength (Å)	s range (Å ⁻¹)
501.278	126	0.049087	1.875–14.25
192.189	126	0.049087	8.75–36.25

Table 2
Optimized geometrical parameters of DCCP by using different levels of theory

	HF/6-31G(d,p)		B3PW91/6-31G(d)		B3PW91/6-311 + G(2df,2pd)		MP2/6-31G(d,p)		MP2/6-311 + G(2df,2pd)	
	C_s	C_2	C_s	C_2	C_s	C_2	C_s	C_2	C_s	C_2
<i>Bond distances (Å)</i>										
C ₁ –C ₂	1.5493	1.5710	1.5562	1.5782	1.5525	1.5736	1.5470	1.5706	1.5443	1.5675
C ₂ –C ₃	1.5385	1.5309	1.5380	1.5303	1.5331	1.5254	1.5364	1.5281	1.5338	1.5256
C ₃ –C ₄	1.5513	1.5284	1.5523	1.5293	1.5477	1.5258	1.5510	1.5263	1.5497	1.5248
q^a	0.414	0.419	0.421	0.421	0.413	0.415	0.440	0.436	0.443	0.446
C ₁ –C ₆	1.4807	1.4778	1.4730	1.4697	1.4674	1.4636	1.4716	1.4686	1.4643	1.4607
C ₁ –C ₈	1.4754	1.4778	1.4673	1.4697	1.4613	1.4636	1.4656	1.4686	1.4580	1.4607
–C≡N	1.1343	1.1344	1.1606	1.1607	1.1499	1.1500	1.1824	1.1824	1.1707	1.1708
⟨C–H⟩ ^b	1.0832	1.0837	1.0942	1.0948	1.0898	1.0904	1.0896	1.0902	1.0882	1.0889
<i>Bond angles (°)</i>										
C ₁ –C ₂ –C ₃	104.1	104.8	104.0	104.8	104.2	105.0	103.4	104.5	103.3	104.4
C ₂ –C ₃ –C ₄	106.2	103.4	106.2	103.4	106.3	103.5	105.9	102.9	105.9	102.6
C ₅ –C ₁ –C ₂	102.1	105.2	101.6	104.8	101.7	104.9	101.5	105.0	101.4	104.9
NC–C–CN	109.1	108.4	109.5	108.8	109.6	109.1	110.1	109.2	110.3	109.3
H–C ₂ –H	108.0	107.8	108.0	107.7	107.9	107.7	108.4	108.0	108.5	108.2
H–C ₃ –H	107.1	107.7	107.0	107.6	106.9	107.5	107.3	107.9	107.3	108.1
β_6^c	123.2	125.8	122.9	125.6	123.0	125.5	121.8	125.4	121.8	125.3
β_8^d	127.7	125.8	127.6	125.6	127.3	125.5	128.1	125.4	127.9	125.3
α^e	40.5		40.9		40.2		43.1		43.5	
η^f	2.1	2.2	2.2	2.2	2.4	2.5	2.6	2.4	2.7	2.5
<i>Dihedral angles (°)</i>										
C ₁ –C ₂ –C ₃ –C ₄	24.9	–34.9	25.2	–35.6	24.9	–34.8	26.4	–36.4	26.6	–37.2
C ₄ –C ₅ –C ₁ –C ₂	40.0	13.3	40.4	12.7	39.8	13.2	42.5	13.8	42.8	14.2
C ₂ –C ₃ –C ₄ –C ₅	0.0	43.7	0.0	44.1	0.0	43.6	0.0	45.6	0.0	46.6
ΔE^g	–	0.993	–	0.572	–	0.287	–	1.523	–	1.049

^a Puckering amplitude for the ring, calculated with program RING [26,27].

^b Average value.

^c Angle between the bond C₆–C₁ and the plane C₅C₁C₂.

^d Angle between the bond C₈–C₁ and the plane C₅C₁C₂.

^e Angle between the C₅C₁C₂ plane and C₂C₃C₄C₅ plane (flap angle).

^f Bending angle (outwards) of the C–C≡N chain.

^g $\Delta E = E(C_2) - E(C_s)$ (kcal/mol).

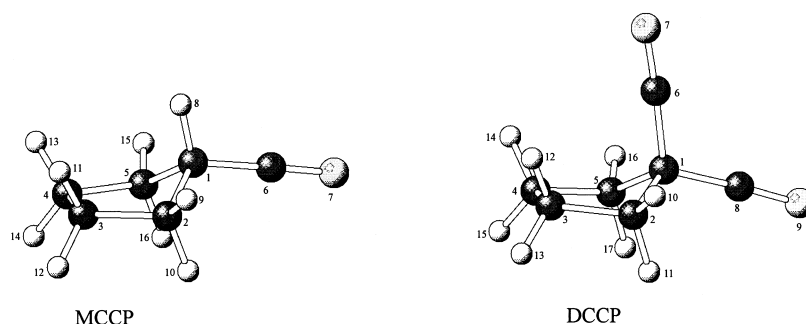


Fig. 1. Atomic numbering of MCCP and DCCP.

Table 2 lists the most prominent structural parameters of DCCP as predicted by the latter four ab initio methods. For atomic numbering see Fig. 1.

4. Static models

Initially we started the analysis of the electron diffraction data by applying static models of symmetry C_s and/or C_2 . Since not all the independent structural parameters of DCCP can be determined from the electron diffraction intensities, the following assumptions were introduced for the data refinement: (1) all geometrical parameters of the $C-C\equiv N$ moieties are equal; (2) all $C-H$ bond distances were assumed to be equal; (3) all $H-C-H$ bond angles were assumed to be equal; and (4) local C_{2v} symmetry was assumed for the CH_2 groups. In addition the overall molecular symmetry implies the constraints $r(C_1-C_2) = r(C_1-C_5)$, $r(C_2-C_3) = r(C_4-C_5)$, $\angle(C_1-C_2-C_3) = \angle(C_4-C_5-C_1)$, and $\angle(C_2-C_3-C_4) = \angle(C_3-C_4-C_5)$. Further we have for C_s symmetry $\angle(C_2-C_3-C_4-C_5) = 0$, $\angle(C_1-C_2-C_3-C_4) = -\angle(C_3-C_4-C_5-C_1)$, $\angle(C_4-C_5-C_1-C_2) = -\angle(C_5-C_1-C_2-C_3)$, and for C_2 symmetry $\angle(C_1-C_2-C_3-C_4) = \angle(C_3-C_4-C_5-C_1)$ and $\angle(C_4-C_5-C_1-C_2) = \angle(C_5-C_1-C_2-C_3)$. When attempting to fit different ratios of C_s and C_2 conformations it was also assumed that the ring $C-C$ bond distances have the same values in both conformations.

To obtain reasonable values for the vibrational amplitudes l_{ij} a normal coordinate analysis has been conducted using the force fields provided by the HF/6-

31G** method for both the C_s and the C_2 forms. The procedure we applied for the determination of these amplitudes has been described previously [7]. It is worthwhile to note that initially the values for several calculated vibrational amplitudes of non-bonded distances were unreasonably high. The subsequent elimination of the contributions from the lowest vibrational frequency, the pseudorotation, however, has led to generally plausible values.

At this stage of the present electron diffraction study it became evident that by applying static models the geometry of DCCP is most properly described when the envelope form (C_s symmetry) was used. Neither the C_2 conformer nor a combination of different ratios of the C_s and C_2 conformers could be adequately described by the electron diffraction data. This result also supports the significant changes in the ring $C-C$ bond lengths in going from C_s to C_2 symmetry which were obtained in the ab initio calculations. This was introduced into the subsequent large amplitude treatment. The predominance of the C_s form is consistent with the results predicted by all ab initio methods that have been applied for this study (Table 2).

The final results of the structural analysis gained from the refinement of the static C_s model are shown in Table 3. In Tables 3 and 5 the different σ values have the following meaning: σ_1 is the single standard error of the fitting procedure, σ_2 is the error propagated from the estimated uncertainties of the fixed parameters, and σ_{total} is the combined final error estimate. The method to calculate the propagated error σ_2 and the total error σ_{total} has been described in Refs. [7–9].

Table 3

Structural parameters (r_a) of DCCP as obtained from the fit of the static C_s model, with different kinds of uncertainties

	r_a	σ_1^a	σ_2^b	σ_{total}^c
Bond distances (\AA)				
C ₁ –C ₂	1.554	0.003	0.003	0.009
C ₂ –C ₃	1.544	0.003	0.004	0.010
C ₃ –C ₄	1.560	fix		
C–C \equiv	1.474	0.001	0.001	0.004
C \equiv N	1.165	0.001	0.001	0.002
C–H	1.088	fix		
Bond angles ($^\circ$)				
NC–C–CN	107.6	0.6	0.8	2.1
γ^d	41.6	0.6	1.1	2.3
C ₂ –C ₃ –C ₄	106.8	0.1	0.2	0.5
H–C–H	111.3	0.6	1.3	2.7
η^e	5.8	0.8	0.7	2.3
ε^f	1.8	0.5	0.4	1.5
Vibrational amplitudes (\AA)				
IC–C _{ring}	0.056	0.001	0.001	0.002
IC–C \equiv	0.044	0.002	0.002	0.005
IC–H	0.078	0.002	0.002	0.006
IC \equiv N	0.031	0.000	0.001	0.002
IC ₂ ...C ₅	0.070	0.017	0.019	0.053
IC ₂ ...C ₆	0.068	0.008	0.012	0.028
IC ₃ ...C ₆	0.267	0.020	0.023	0.064
IC ₃ ...C ₈	0.090	0.005	0.002	0.012
IC ₂ ...N ₇	0.114	0.007	0.005	0.019
IC ₃ ...N ₇	0.344	0.042	0.025	0.111
IC ₃ ...N ₉	0.121	0.005	0.001	0.012
IC ₆ ...N ₉	0.095	0.007	0.006	0.019
IN...N	0.156	0.015	0.013	0.044
IC ₁ ...H ₁₀	0.111	0.002	0.001	0.004
R_{long}^g	2.02			
R_{short}^g	3.59			

^a σ_1 is the single standard error of the fit.

^b σ_2 is the propagated error [7–9].

^c $\sigma_{\text{total}} = \sqrt{6\sigma_1^2 + 3\sigma_2^2}$.

^d The angle between the C₅–C₁–C₂ plane and the C₂C₃C₄C₅ plane (flap angle).

^e Bending angle (outwards) of the C–C \equiv N chain.

^f Rocking angle of the NC–C–CN group.

^g $R = 100[\sum w_i \Delta_i^2 / \sum (w_i s^2 M_i^2(\text{obs}))]^{1/2}$,

where $\Delta_i = sM_i(\text{obs}) - sM_i(\text{calc})$.

5. Large amplitude treatment

Saturated five-membered rings are known to undergo a special form of vibrational motion, the pseudorotation [10–12]. A close examination of the variation of non-bonded distances during one cycle of pseudorotation shows that in DCCP the intramole-

cular distances for several pairs of atoms change by up to 2 \AA . This indicates that the analysis of the experimental data using a large amplitude treatment of the pseudorotation should be more appropriate than a static model allowing only for C_s symmetry.

In 1,1-disubstituted five-membered rings the pseudorotational motion is characterized by a potential function of the form (neglecting higher terms)

$$V(\phi) = \frac{1}{2} V_2(1 - \cos 2\phi) + \frac{1}{2} V_4(1 - \cos 4\phi)$$

where ϕ is the phase of the pseudorotation. This gives stable configurations of C_s symmetry at $\phi = 0, \pm\pi, \pm2\pi, \dots$, and stable configurations of C_2 symmetry at $\phi = \pm\pi/2, \pm3\pi/2, \dots$. The energy difference between the minima of the potential function is given by the constant V_2 . Fig. 2 shows the potential function for 1,1-dicyanocyclopentane.

To account for large amplitude motions in the analysis of gas-phase electron diffraction data the assumption is made that the large amplitude motion is a slow motion, and the reduced total molecular intensity $sM(s)$ can be written as [13,14]

$$sM(s)_{\text{total}} = \int_0^{2\pi} w(\phi) sM(s, R(\phi)) d\phi / \int_0^{2\pi} w(\phi) d\phi \quad (1)$$

where $R(\phi)$ designates the geometry of the molecule at the phase angle ϕ . The weight function $w(\phi)$ at temperature T with normalizing factor N is given by

$$w(\phi) = N \exp(-V(\phi)/RT)$$

To apply these formulas to DCCP various problems have to be solved. Most importantly the dependency of the geometry on the phase angle ϕ should be analyzed. Inspection of Table 2 shows that the ring C–C bond distances as obtained from ab initio calculations depend strongly on the phase angle ϕ : the C₁–C₂ distance increases by about 0.023 \AA in going from $\phi = 0$ to $\pi/2$ and thereby the C₃–C₄ distance decreases by 0.024 \AA . We would like to note that similar calculations for 1,1-dichlorocyclopentane [15] show an analogue behavior. With a slight modification of Eq. (2) this procedure has proven to be also applicable to five-membered rings including heteroatoms like Silacyclopentane [16]. However, in the large amplitude analysis of the diffraction patterns it is required to establish the ring geometry for any phase angle ϕ . Therefore we rationalize this observation by using the following model: in contrast to the

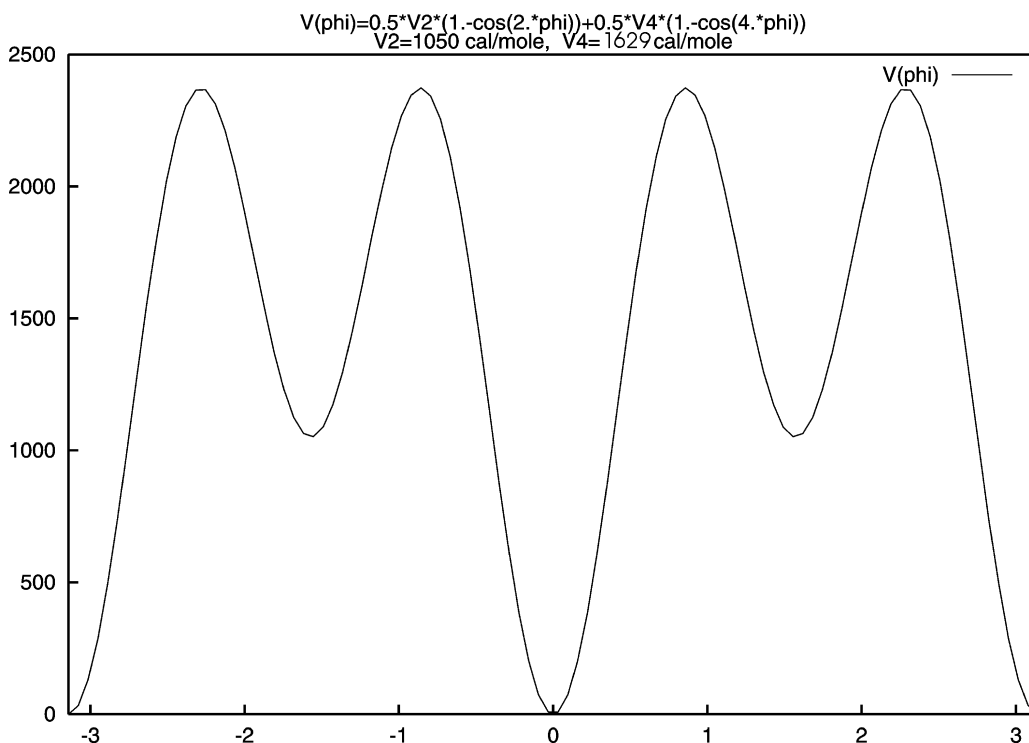


Fig. 2. Potential function of pseudorotation for 1,1-dicyanocyclopentane (angles in radian). $V_2 = 1050$ cal/mol is the energy difference between the C_s and the C_2 configuration as calculated by MP2/6-311 + G(2df,2pd), $V_4 = 1629$ cal/mol is the final fitted value from the r_α fit.

localized electron density distribution the density distribution of the delocalized net charges which represents the overall distribution of charges throughout the ring depends markedly on the phase angle ϕ . Assuming that this dependency for the C_s and C_2 conformers can be described by a function of the form shown in Fig. 3 we may write for the density distribution

$$d(\alpha, \phi) = d_1 \cos \alpha + d_2 \cos 2\alpha + d_\phi \cos \alpha \cos 2\phi \quad (2)$$

where α designates the angle between the axis from the center of the ring to atom C_1 and every position along the ring, both projected to the mean plane as defined by Cremer and Pople [27]. The coefficients d_1 , d_2 , and d_ϕ are adjustable parameters. Therefore, the contribution of the delocalized net charges to the bond distance C_i – C_j can be written as

$$r_{ij} = r_{CC} + \int_{\alpha_i}^{\alpha_j} d(\alpha, \phi) d\alpha \quad (3)$$

Assuming a regular pentagon in the mean plane of the five-membered ring the integral can be easily evaluated. If we neglect the differences in the puckering amplitudes q resulting for the C_s and C_2 forms and adjust the parameters r_{CC} , d_1 , d_2 , and d_ϕ to the ab initio distances for both symmetries by applying a least squares procedure we obtain the results listed in Table 4. It can easily be seen from Table 2 and Eq. (3) that r_{CC} is the mean value of the ring C–C bond distances.

Since the largest deviation from the ab initio values is 0.001 \AA we adopted the coefficients d_1 , d_2 , and d_ϕ as well as the values of the integrals $\int_{\alpha_i}^{\alpha_j} \cos \alpha d\alpha$ and $\int_{\alpha_i}^{\alpha_j} \cos 2\alpha d\alpha$ for fitting the geometry by using the electron diffraction data. The ring distances were calculated according to

$$r_{12} = r_{CC} + 0.951057d_1 - 0.293893d_2 + 0.951057d_\phi \cos 2\phi \quad (4)$$

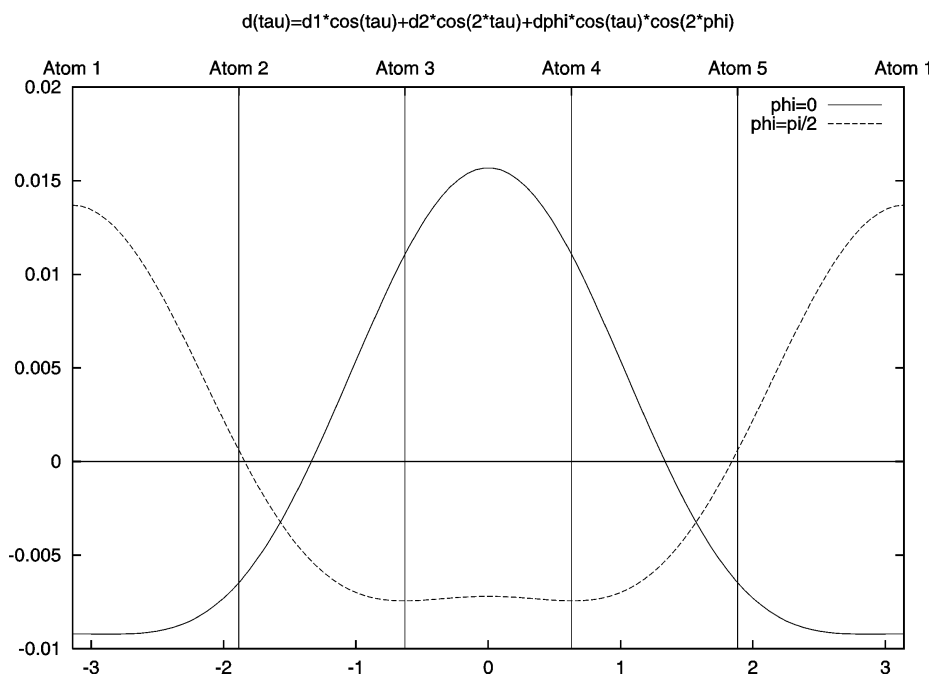


Fig. 3. Density of delocalized net charge distribution for $\phi = 0$ (—) and $\phi = \pi/2$ (---) (angles in radian).

$$r_{23} = r_{CC} - 0.363271d_1 + 0.769421d_2 - 0.363271d_\phi \cos 2\phi \quad (5)$$

$$r_{34} = r_{CC} - 1.175571d_1 - 0.951057d_2 - 1.175571d_\phi \cos 2\phi \quad (6)$$

Further inspection of Table 2 shows that the bond angle $C_5-C_1-C_2 = \alpha_{512}$ differs by more than 3° for

the conformations with C_s and C_2 symmetry. This was taken into account by using

$$\alpha_{512}(\phi) = \alpha_{512}(C_s) + \delta_{512}(1 - \cos 2\phi)/2 \quad (7)$$

To set up the geometry of the ring we additionally made use of the formula given by Kilpatrick et al. [17] for the z coordinates of the ring atoms

$$z_i = \sqrt{2/5}q \cos(\phi + 4\pi(i-1)/5) \quad i = 1, \dots, 5 \quad (8)$$

Table 4

Fitted constants from Eq. (2) and ring C–C bond distances calculated from Eqs. (4)–(6) for 1,1-dicyanocyclopentane

	HF/6-31G(d,p)		B3PW91/6-31G(d)		MP2/6-31G(d,p)		MP2/6-311+G(2df,2pd)	
<i>Fitted constants</i>								
r_{CC}	1.54561(54)		1.54868(53)		1.54413(60)		1.54166(49)	
d_1	0.01205(61)		0.01591(62)		0.01245(68)		0.01188(56)	
d_2	−0.00862(76)		−0.01137(76)		−0.00963(84)		−0.01000(69)	
d_ϕ	−0.01041(58)		−0.01047(58)		−0.01126(64)		−0.01126(53)	
<i>C–C distances calculated from Eqs. (4)–(6)</i>								
	C_s	C_2	C_s	C_2	C_s	C_2	C_s	C_2
C_1 – C_2 , C_1 – C_5	1.5497	1.5695	1.5572	1.5771	1.5481	1.5695	1.5452	1.5666
C_2 – C_3 , C_4 – C_5	1.5384	1.5308	1.5380	1.5303	1.5363	1.5281	1.5337	1.5256
C_3 – C_4	1.5519	1.5274	1.5531	1.5285	1.5519	1.5254	1.5504	1.5240

The same q was used for all values of ϕ . The calculation of the ring geometry is completed using a coordinate system with the x and y axes lying in the ring mean plane: the coordinate system is chosen such, that the projection of atom C_1 into the mean plane, lies on the x axis, and the origin is positioned so that all angles from one edge of the planar pentagon to an adjacent edge is 72° . Thus, if we fix d_1 , d_2 , and d_ϕ to the values given in the last column of Table 4 and δ_{512} to the ab initio value, only r_{CC} , α_{512} , and q are free parameters at a given phase angle ϕ for fitting the ring geometry.

Further, we observed a strong dependency of the $C_1-C\equiv$ distance as well as the $C(C\equiv N)_2$ rocking angle ρ on the phase angle ϕ . The difference in the *axial* and *equatorial* $C_1-C\equiv$ bond distances is found to be ~ 0.006 Å, and the rocking angle $\sim 2.7^\circ$ in C_s form. However, the twisting τ of the $C(C\equiv N)_2$ group in the C_2 conformer is only $\sim 0.3^\circ$. These dependencies were taken into account by applying the following equations:

$$r_{C_1-C\equiv} = r_{CC\equiv} \pm \delta r_{CC\equiv} \cos \phi, \quad \rho(\phi) = \rho \cos \phi,$$

$$\tau(\phi) = \tau \sin \phi$$

A dependency of the geometry of the methylene groups on ϕ , though present in the ab initio results, was not taken into consideration because the sensitivity of the diffraction data on these parameters is too small: the rocking, wagging, and twisting angles were fixed to zero, and all C–H distances were assumed to be equal.

A second problem to be solved is the correlation between the root mean square amplitudes l_{ij} and the phase angle ϕ . Using the scaled quadratic ab initio force fields for both stable conformations C_s and C_2 we have calculated the vibrational amplitudes within the range $-\pi \leq \phi < +\pi$ with a step width of $\delta\phi = 9^\circ$. Following Hilderbrandt et al. [18] we tried to establish with these data a dependency of the vibrational amplitudes on ϕ of the form

$$l_{ij} = l_{ij}^0 + a(1 - \cos \phi)$$

However it turned out that there is no such simple dependency for most of the l_{ij} . This is demonstrated for some examples in Fig. 4 utilizing the vibrational amplitudes $l(C_3\cdots N_7)$, $l(C_4\cdots N_7)$, $l(N_7\cdots H_{12})$, and

$l(N_7\cdots H_{14})$ and the corresponding distances. We therefore decided to use the differences $l_{ij}(\phi \neq 0) - l_{ij}(\phi = 0)$ of the calculated vibrational amplitudes: these were introduced into the analyzing programs as constants to be added to the vibrational amplitudes of the most stable conformer (symmetry C_s at $\phi = 0$). This limits the possibility to adjust the vibrational amplitudes in the least squares procedure to cases where the scatter of the calculated amplitudes is sufficiently small. Values at intermediate ϕ are obtained by interpolation.

To calculate $sM(s)_{\text{total}}$ from Eq. (1) we used the usual assumption that the integral can be approximated sufficiently well by finite sums. Therefore the geometry of the molecule was set up for various values of the phase angle ϕ , and the corresponding $M(s, R(\phi))$ was calculated. For symmetry reasons it is sufficient to use an interval width of π . We used a step width of $\delta\phi = 5^\circ$ in the interval $-135 \leq \phi \leq +45^\circ$, giving a total of 37 intermediate conformers.

Attempts have been undertaken to extract the potential constants V_2 and V_4 from the experimental gas electron diffraction data. However, it turned out, that the dependence of the data on V_2 and V_4 is very poor. Therefore, the constant V_2 was fixed at the ab initio energy difference between the conformers of C_s and C_2 symmetry, and only V_4 was adjusted.

Using the pseudorotational model two different types of fitting schemes have been applied to deduce the molecular structure from the electron diffraction patterns: in a first attempt an r_a structure was fitted under the assumption that the r_a parameters are geometrically consistent. Though the overall fit is acceptable, several problems cannot be solved sufficiently well, however. In particular the discrepancy between the experimental and theoretical radial distribution curve in the region at 4.0 Å (Fig. 6) is too large, and also the deviation of the C–C≡N chain from linearity by 6.9° is not acceptable. Since it is well known that in molecules containing linear chains the perpendicular vibrational amplitudes contribute significantly to the non-bonded r_a distances, we decided to fit the r_α geometry, which is geometrically consistent by definition. The required corrections ($r_a - r_\alpha$) were calculated along with the vibrational amplitudes by using the force field provided from the HF/6-31G** calculations. These data were entered as additional constants. The results of both types of fitting are listed in Table 5.

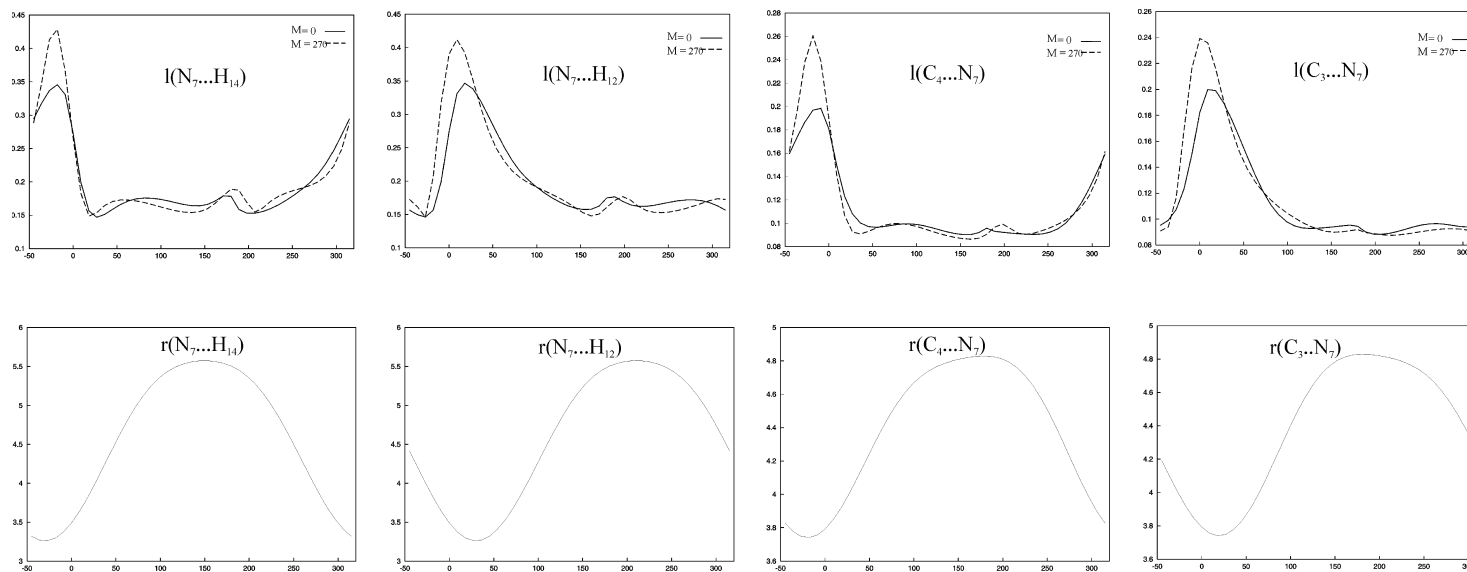


Fig. 4. Dependency of selected vibrational amplitudes (upper row) and corresponding distances (lower row) on phase angle ϕ . Calculations were performed with the scaled ab initio force fields obtained at $\phi = 0^\circ$ (C_s symmetry, —) and at $\phi = 270^\circ$ (C_2 symmetry, - - -).

Table 5

Final model parameters (r_a , r_α) and errors for 1,1-dicyanocyclopentane using the pseudorotational model. The parameters d_1 , d_2 , and d_ϕ are the respective coefficients in Eqs. (4)–(6)

	r_a fit				r_α fit			
	Value	σ_1^a	σ_2^b	σ_{total}^c	Value	σ_1^a	σ_2^b	σ_{total}^c
<i>Geometrical parameters (distances in Å, angles in °)</i>								
C–C _{ring}	1.552	0.001	0.001	0.003	1.549	0.001	0.001	0.003
d_1	0.0119	fix			0.0119	fix		
d_2	−0.0100	fix			−0.0100	fix		
d_ϕ	−0.0113	fix			−0.0113	fix		
q^d	0.419	0.016	0.017	0.049	0.434	0.018	0.014	0.051
C–C'	1.472	0.002	0.002	0.006	1.472	0.002	0.002	0.005
dC–C'	−0.011	0.020	0.014	0.055	−0.0065	fix		
C–N	1.164	0.001	0.001	0.002	1.152	0.001	0.001	0.002
C–H	1.085	0.002	0.001	0.004	1.068	0.002	0.001	0.004
C ₅ –C ₁ –C ₂	104.6	1.0	1.1	3.2	103.6	1.1	0.9	3.1
δ_{512}	3.50	fix			3.50	fix		
NC–C–CN	108.9	0.8	1.4	3.1	109.1	1.2	1.2	3.7
H–C–H	113.1	1.0	0.5	2.7	112.6	0.9	0.5	2.3
C–C–N	173.1	1.2	0.9	3.2	175.2	1.2	0.9	3.4
ρ^e	−6.7	2.3	2.4	7.0	−4.1	2.1	1.4	5.6
τ^f	0.31	fix			0.31	fix		
<i>Fitted vibrational amplitudes (Å)</i>								
IC–C _{ring}	0.054	0.001	0.001	0.004	0.055	0.001	0.001	0.003
IC–C•	0.041	0.005	0.002	0.012	0.041	0.002	0.002	0.006
IC–H	0.079	0.003	0.001	0.007	0.076	0.002	0.001	0.006
IC•N	0.030	0.001	0.000	0.002	0.029	0.001	0.000	0.002
IC ₂ ••C ₄	0.064	0.012	0.008	0.032	0.071	0.013	0.017	0.044
IC ₂ ••C ₈	0.068	0.009	0.010	0.027	0.070	0.008	0.010	0.026
IC ₃ ••C ₈	0.073	0.005	0.004	0.014	0.075	0.005	0.002	0.013
IC ₂ ••N ₉	0.101	0.008	0.012	0.029	0.104	0.004	0.007	0.015
IC ₃ ••N ₉	0.113	0.009	0.004	0.022	0.111	0.008	0.003	0.020
IC ₁ ••H ₁₀	0.112	0.002	0.001	0.006	0.111	0.002	0.001	0.005
<i>Potential constants (cal/mol)</i>								
V ₂	1050	fix			1050	fix		
V ₄	1469	865	945	2677	1629	1150	963	3274
R _{long}	3.41				2.89			
R _{short}	3.99				3.81			

^a σ_1 is the single standard error of the fit.

^b σ_2 is the propagated error [7–9].

^c $\sigma_{\text{total}} = \sqrt{6\sigma_1^2 + 3\sigma_2^2}$.

^d Puckering amplitude.

^e Rocking angle of the NC–C–CN group at C_s symmetry.

^f Twisting angle of the NC–C–CN group at C_2 symmetry.

Figs. 5 and 6 show the experimental and theoretical reduced molecular intensity $sM(s)$, and the experimental and theoretical radial distribution function from the pseudorotational model, respectively. Table 6 shows a comparison of the geometrical parameters which have been obtained from the electron diffrac-

tion investigation with those obtained from the ab initio calculations at the MP2/6-311 + G(2df,2pd) level.

The electron diffraction intensity data, the calculated vibrational amplitudes and the corrections ($r_a - r_\alpha$) are deposited as supplemental data.

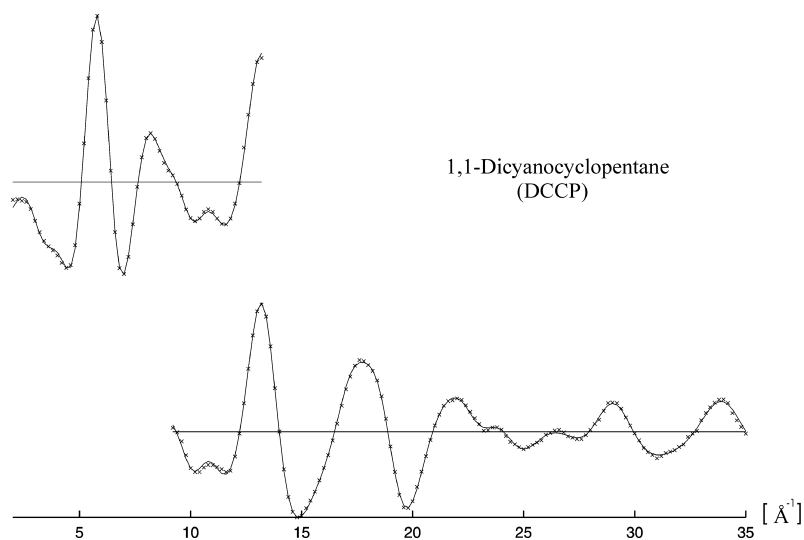


Fig. 5. Experimental (x) and theoretical (—) reduced molecular intensity $sM(s)$ for DCCP.

6. Discussion

Searching for the factors affecting the ring geometry and the symmetry of the five-membered ring in DCCP as a result of the substitution by geminal

cyano groups we found it reasonable to carry out ab initio calculations on monocyano cyclopentane (MCCP) and to compare the results with those of DCCP. For a proper comparison we used the same methods and basis sets we employed in the case of

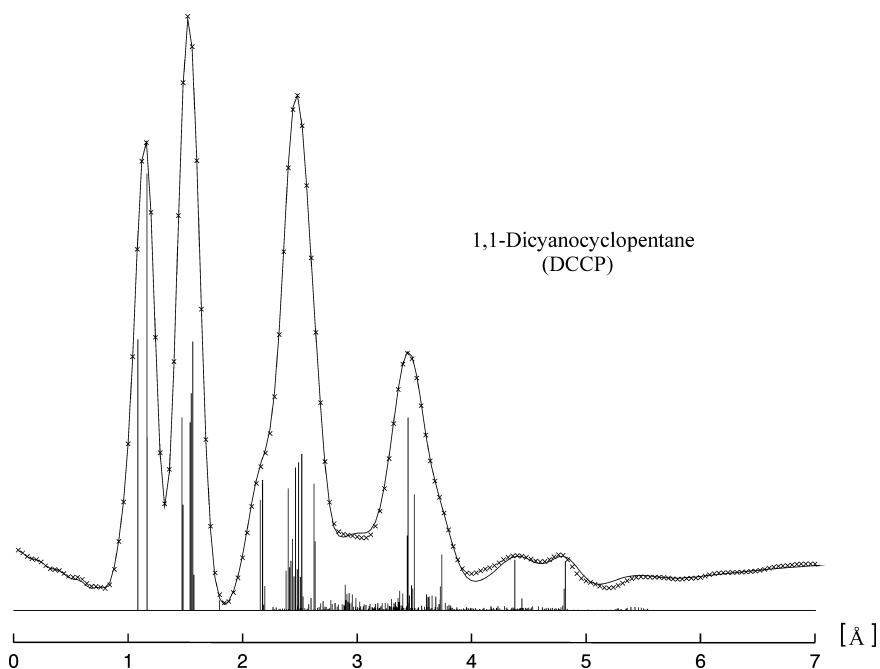


Fig. 6. Experimental (x) and theoretical (—) radial distribution function from pseudorotational model for DCCP.

Table 6

Comparison of r_a distances, bond angles and dihedral angles of 1,1-dicyanocyclopentane (DCCP) as obtained from electron diffraction and ab initio calculations (MP2/6-311 + G(2df,2pd))

	C_s only	r_a fit		r_a fit		Ab initio	
	C_s	C_s	C_2	C_s	C_2	C_s	C_2
<i>Bond distances</i> (Å)							
C_1-C_2	1.554	1.556	1.577	1.555	1.576	1.5443	1.5675
C_2-C_3	1.544	1.545	1.536	1.548	1.535	1.5338	1.5256
C_3-C_4	1.560	1.561	1.535	1.558	1.536	1.5497	1.5248
q^a	0.418	0.419	0.419	0.434	0.434	0.443	0.446
$C_1-C_6\equiv$	1.474	1.482	1.472	1.482	1.475	1.4643	1.4607
$C_1-C_8\equiv$	1.474	1.461	1.472	1.469	1.475	1.4580	1.4607
$-C\equiv N$	1.165	1.164	1.164	1.165	1.164	1.1707	1.1708
$\langle C-H \rangle^b$	1.088	1.085	1.085	1.084	1.083	1.0882	1.0889
<i>Bond angles</i> (°)							
$C_1-C_2-C_3$	102.3	101.8	102.5	102.0	103.0	103.3	104.4
$C_2-C_3-C_4$	106.7	107.0	104.3	106.6	103.6	105.9	102.6
$C_5-C_1-C_2$	104.0	104.6	108.1	103.6	107.1	101.4	104.9
$NC-C-CN$	107.6	108.9	108.9	109.1	109.1	110.3	109.3
$H-C-H$	111.3	113.1	113.1	112.6	112.6	107.9	108.2
β_6^c	128.6	118.8	125.6	121.4	125.5	121.8	125.3
β_8^d	122.7	132.3	125.6	129.5	125.5	127.9	125.3
α^e	41.6	41.9	—	43.1	—	43.5	—
η^f	5.8	6.9	6.9	4.8	4.8	2.7	2.5
<i>Dihedral angles</i> (°)							
$C_1-C_2-C_3-C_4$	24.7	24.6	− 34.5	25.6	− 35.8	26.6	− 37.2
$C_4-C_5-C_1-C_2$	40.6	40.7	13.1	42.0	13.6	42.8	14.2
$C_2-C_3-C_4-C_5$	0.0	0.0	44.5	0.0	45.8	0.0	46.6

^a Puckering amplitude for the ring.

^b Average value.

^c Angle between the bond C_6-C_1 and the plane $C_5C_1C_2$.

^d Angle between the bond C_8-C_1 and the plane $C_5C_1C_2$.

^e Angle between the $C_5C_1C_2$ plane and $C_2C_3C_4C_5$ plane (flap angle).

^f Bending angle (outwards) of the $C-C\equiv N$ chain.

DCCP. Additionally, the optimized geometry of MCCP by using the basis set 6-311++G(2df,2pd) and the B3PW91 and the MP2 methods has been calculated.

Before comparing the ab initio results we would like to discuss very briefly the conformational preference in MCCP and to address the controversy which has arisen about the occurrence of the axial and equatorial conformers in this molecule. The second order Møller–Pleset perturbation theory by using the basis sets 6-31G(d,p), 6-311 + G(2df,2pd), and 6-311++G(d,p) has shown that MCCP exists in axial and equatorial forms with the axial conformer lower in energy by 0.415, 0.370, and 0.535 kcal/mol, respec-

tively, and thus being the more stable conformer. In contrast, the Hartree–Fock method UHF/6-31G(d,p) has suggested the equatorial conformer to be more stable by 0.360 kcal/mol. Similarly, the density functional (DFT) hybrid method B3PW91 in combination with the basis sets 6-311++G(df,pd) and 6-311++G(2df,2pd) favors the equatorial conformer by 0.361 and 0.466 kcal/mol, respectively. This result is interesting because it reflects the confusion that took place concerning the conformational stability of MCCP as it was found by the experimental studies. A microwave investigation carried out by Choe and Harmony [19] could not provide clear cut evidence for the preference of one or the other conformer and,

Table 7
Optimized geometrical parameters of MCCP (envelope C_s symmetry)

	HF/6-31G(d,p)		B3PW91/6-311++G(2df,2pd)		MP2/6-31G(d,p)		MP2/6-311++G(2df,2pd)		Exp. ^a
	eq	ax	eq	ax	eq	ax	eq	ax	
<i>Bond distances (Å)</i>									
C ₁ –C ₂	1.5372	1.5393	1.5378	1.5403	1.5362	1.5377	1.5334	1.5356	1.544(1) ^b
C ₂ –C ₃	1.5394	1.5403	1.5351	1.5363	1.5372	1.5381	1.5351	1.5362	
C ₃ –C ₄	1.5524	1.5514	1.5492	1.5481	1.5513	1.5507	1.5505	1.5497	
<i>q</i> ^c	0.414	0.398	0.412	0.395	0.431	0.426	0.439	0.432	0.426(28)
C–C≡	1.4713	1.4771	1.4531	1.4592	1.4616	1.4672	1.4537	1.4597	1.477(7)
–C≡N	1.1356	1.1358	1.1512	1.1514	1.1817	1.1818	1.1704	1.1706	1.160(2)
C ₁ –H	1.0866	1.0839	1.0954	1.0921	1.0944	1.0913	1.0931	1.0894	
⟨C–H⟩	1.0852	1.0840	1.0908	1.0905	1.0901	1.0900	1.0887	1.0886	1.102(6)
<i>Bond angles (°)</i>									
C ₁ –C ₂ –C ₃	103.5	104.6	103.7	104.7	103.3	103.8	103.1	103.7	
C ₂ –C ₃ –C ₄	106.1	106.0	106.2	106.1	105.9	105.8	105.8	105.7	
C ₅ –C ₁ –C ₂	102.9	102.5	102.8	102.3	102.4	101.9	102.1	101.7	
H–C ₁ –C≡	107.2	107.1	107.4	107.3	108.2	108.5	108.3	108.5	
C _{2,5} –C ₁ –C≡	113.8	111.2	114.1	111.6	113.9	110.5	113.8	110.3	112.1(13)
⟨H–C–H⟩	107.2	107.7	107.0	107.2	107.4	107.6	107.5	107.7	107.2(32)
<i>β</i> ₆ ^d	130.5	125.2	130.9	125.9	130.4	123.8	129.9	123.4	
<i>β</i> ₈ ^e	122.4	127.6	121.7	126.8	121.4	127.7	121.8	128.1	
<i>α</i> ^f	41.2	39.1	40.8	38.8	42.7	42.0	43.5	42.6	
<i>Dihedral angles (°)</i>									
C ₁ –C ₂ –C ₃ –C ₄	24.9	24.1	24.8	24.0	25.9	25.7	26.4	26.1	
C ₄ –C ₅ –C ₁ –C ₂	40.6	38.8	40.2	38.5	42.0	41.5	42.9	42.1	

^a Pseudorotating model given in Ref. [18] (r_g values).

^b Single average C–C bond.

^c Puckering amplitude for the ring, calculated with program RING [26,27].

^d Angle between the bond C₆–C₁ and the plane C₅C₁C₂.

^e Angle between the bond H₈–C₁ and the plane C₅C₁C₂.

^f Angle between the C₅C₁C₂ plane and C₂C₃C₄C₅ plane (flap angle).

therefore, the authors suggested that both conformers might be energetically equally favored. However, Hilderbrandt et al. [18] concluded from their electron diffraction data that the equatorial conformer is by 180(330) cal/mol preferred over the axial form. Based on our ab initio results presented in this work we conclude that the axial conformer in MCCP is energetically more stable and the prediction by the HF and DFT methods are less reliable. Perhaps it is of interest to indicate that the predicted dipole moments for the axial and equatorial conformers differ only by about 0.3 D.

Further discrepancies between the electron diffraction and the quantum mechanical results are visible from the C–C≡ and C≡N bond lengths. As it is shown in Table 7 the experimentally determined C–C≡ bond

length in MCCP is about 0.02 Å longer than predicted by the MP2/6-311++G(2df,2pd) and B3PW91/6-311++G(2df,2pd) methods. On the other hand the experimental value for the C≡N bond is by 0.01 Å shorter than that produced by the MP2 method and by 0.01 Å longer than it has been predicted by the DFT method. The value of 1.1356 Å for this bond as predicted by the HF/6-31G(d,p) calculations is definitely too low.

Overall, based on the ab initio results presented in this work a closer scrutiny of the conformational analysis by the experiment seems to be warranted.

Consistently, all ab initio methods we applied show that the ring geometrical parameters remain almost unchanged upon going from the axial to the equatorial conformer. It is also remarkable that the exocyclic

angle $\text{H}-\text{C}_1-\text{C}\equiv$ and the bond lengths within the $\text{C}-\text{C}\equiv\text{N}$ moiety are negligibly different in both conformers. Only the flap angle is approximately 1° smaller in the axial conformer. All these findings explain the uncertainty of the microwave and electron diffraction experiments by the determination of the conformational stability for M CCP.

From Table 2 it is evident that for D CCP the agreement between the values produced by the ab initio methods we used in the present study is fairly good. Nevertheless, a closer consideration of the various parameters shown in Table 2 indicates that the C_1-C_2 bond is slightly overestimated by the DFT method and both the DFT and $\text{HF}/6\text{-}31\text{G}^{**}$ methods overestimate the C_1-C_6 bond. It is also worthwhile to note that the $\text{HF}/6\text{-}31\text{G}^{**}$ level of theory overestimates the C_1-C_8 bond length but it drastically underestimates (rather more than the DFT method) the $\text{C}\equiv\text{N}$ bond distance.

A comparison between the ab initio results which have been produced by the $\text{MP2}/6\text{-}311 + \text{G}(2\text{df},2\text{pd})$ method for the envelope form of D CCP and the predominant axial conformer of M CCP (Tables 2 and 7) leads to the following conclusions: (i) While the vicinal ring carbon-carbon bond increases by about 0.01 \AA upon going from M CCP to D CCP the remaining ring $\text{C}-\text{C}$ bonds, however, stay almost unchanged. (ii) The equatorial $\text{C}-\text{C}\equiv$ bond in D CCP is slightly shorter (by 0.006 \AA) than that in axial position and this difference parallels the difference between the axial and equatorial $\text{C}-\text{C}\equiv$ distance in M CCP. (iii) The computed $\text{C}\equiv\text{N}$ bond does not vary on moving from M CCP to D CCP. (iv) The puckering amplitude q for D CCP is larger than that for M CCP.

From Table 2 it can be easily seen that by applying the MP2 method and the augmentation of the basis set using triple zeta basis set and adding diffuse functions to the heavy atoms and orbitals of higher angular momentum to the heavy atoms and the hydrogens leads generally to a reduction of all bond distances in D CCP. On the other hand, all bond angles remain almost unchanged upon the extension of the basis set. Moreover, it is noticeable that the contraction of the bond lengths within the cyano groups is evident. The $\text{C}-\text{C}\equiv$ and $\text{C}\equiv\text{N}$ bonds shorten by about 0.007 and 0.012 \AA , respectively, due to the augmentation of the basis set.

It is well known that a single bond adjacent to a

triple bond is significantly shortened. This bond shortening has been the focal point of controversial discussions and various concepts of rationalizations have been proposed. Based on Mulliken electron charge density distribution analysis Politzer et al. [20] have found that a significant fraction of the π -electrons of the carbon triple bond is spread over the neighbouring regions (denoted 'outer' π charge). Conclusively, the strengthening of the adjacent single bond is attributed to addition of partial π bonding to the single bond. Although this concept neglects a probable charge polarization effect exerted by the attached substituents it seems to be applicable to the $\text{C}-\text{C}\equiv$ bonds in D CCP.

From the experimental and the ab initio results listed in Tables 2 and 5 it can be easily concluded that the simultaneous lengthening of the $\text{C}\equiv\text{N}$ bonds and shortening of the $\text{C}-\text{C}\equiv$ bonds are adequately describable by the notion of Politzer et al. [20]. Taking this notion into consideration the subsequent electronic contact of the outer π charges in the single bond regions leads to a conjugative or resonance interaction between the geminal cyano groups. Such kind of interaction results in a reduction of the $\text{C}-\text{C}\equiv$ bonds and elongation of the $\text{C}\equiv\text{N}$ bonds as it has been observed in D CCP.

From Tables 2 and 5 it can also be seen that there is quite good agreement between the calculated and the experimental values for the puckering amplitude q .

The relatively large exocyclic $\equiv\text{C}-\text{C}-\text{C}\equiv$ angle is probably the result of the steric repulsion between the geminal cyano groups. Also it is most likely that this repulsive interaction is responsible for the outward bending of the $\text{C}-\text{C}\equiv\text{N}$ chains by about 2.3 and 4.8° as provided by the theory and experiment, respectively. It is important to indicate that this consistency between theory and experiment demonstrates that this bending angle is not the consequence of vibrational effects.

From all the foregoing it may be concluded that the insertion of a second cyano group in geminal position into M CCP does not lead to drastic changes in the geometrical parameters of D CCP. Only the $\text{C}-\text{C}$ bond distances and bond angles associated with the central atom C_1 are influenced by the geminal substitution. The widening of the $\equiv\text{C}-\text{C}-\text{C}\equiv$ angle and the deviation of the $\text{C}-\text{C}\equiv\text{N}$ groups from linearity are due to internal steric repulsion within the $\text{N}\equiv\text{C}-\text{C}-\text{C}\equiv\text{N}$ moiety.

In order to find more pertinent reasons for the non-linearity of the $\text{C}-\text{C}\equiv\text{N}$ moiety in DCCP we performed a natural population analysis (NPA) [21–23] and Mulliken population analysis (MPA) for the C_s and C_2 symmetric forms of DCCP as well as for the axial and equatorial conformers in MCCP. For this purpose we applied the MP2/6-311++G(2df,2pd), MP2/6-311+G(d,p), MP2/6-311G(d,p), and B3PW91/6-311+G(2df,2pd) methods. Without going into further details we summarize the results as follows: As it was anticipated both analyses provided inconsistent charge distributions. For brevity we would like to focus only on the charge distribution on the atoms within the $\text{C}(\text{C}\equiv\text{N})_2$ fragment. While the MPA places negative charges on both atoms in the $\text{C}\equiv\text{N}$ group and positive charge on the anchor atom C_1 , the NPA predicts that the terminal atoms in the $\text{C}-\text{C}\equiv\text{N}$ group are negatively charged and the middle carbon atom is positively charged. It is worthwhile to note that similar contradictory charge distribution was observed for the $\text{C}-\text{C}\equiv\text{N}$ group in both the axial and equatorial conformers in MCCP.

It is generally accepted that the MPA exhibits various fundamental deficiencies [24,25]. One of the major weaknesses of MPA is its dependence on the kind and size of the basis set in use, and one further considerable deficiency is that it partitions in some cases the electronic charges in such a way that negative orbital population occurs. Moreover, in many cases the MPA overestimates the covalent character of a bond although it is ionic. The latter shortcoming of MPA is evident in the equatorial form of MCCP. While the charge distribution for the $\text{C}-\text{C}\equiv\text{N}$ group (using the MP2/6-311+G(d,p) method) according to MPA is $\text{C}(+1.91)-\text{C}(-0.66)\equiv\text{N}(-0.22)$, the NPA, however, results in $\text{C}(-0.27)-\text{C}(+0.34)\equiv\text{N}(-0.33)$. From this example it is evident that in contrast to NPA the MPA suppresses the ionicity of the $\text{C}\equiv\text{N}$ bond. Perhaps the most intriguing feature which emerges from this population analysis for DCCP is the following: Taking the Mulliken charge distribution within the $\text{C}(\text{CN})_2$ fragment into consideration ($\text{N}^-\equiv\text{C}^--\text{C}^+-\text{C}\equiv\text{N}^-$) we may conclude that a considerable repulsive steric interaction due to the negatively charged cyano groups would be dominant leading to a distinct widening of the $\equiv\text{C}-\text{C}-\text{C}\equiv$ angle and to a more accentuated bending of the $\text{C}-\text{C}\equiv\text{N}$ chain. However, in the present study both the experi-

ment and ab initio calculations provide values for the $\equiv\text{C}-\text{C}-\text{C}\equiv$ angle which are close to the magnitude of the tetrahedral angle and the bending angle is relatively small. The charge distribution $\text{N}^-\equiv\text{C}^+-\text{C}^--\text{C}^+\equiv\text{N}^-$ according to NPA elucidates unambiguously these results and justifies the predicted conjugation between the geminally substituted cyano groups. In this case the attractive Coulombic interaction between the positively charged carbon of one cyano group and the negatively charged nitrogen of the other cyano group compensates partially for the repulsive interaction between equally charged atoms in the cyano groups. Such intramolecular interaction antagonizes larger $\equiv\text{C}-\text{C}-\text{C}\equiv$ and $\text{C}-\text{C}\equiv\text{N}$ angles.

Focusing on the most stable envelope (C_s) conformation, the average value for the ring $\text{C}-\text{C}$ bond distances in DCCP emerging from the ab initio calculations (Table 2) agree well with the r_α value resulting from the experimental and ab initio joint analysis. It is also worth to recognize that the averaged $\text{C}-\text{C}\equiv$ bond distance provided by the MP2 method is 0.01 Å shorter than that obtained from the experiment, whereas the average value produced by the DFT method agrees fairly well with the experimental value. The application of the MP2 method and the basis sets 6-31G(d,p) and 6-311 + G(2df,2pd) leads to a $\text{C}\equiv\text{N}$ bond length which is considerably longer than the experimental value by 0.030 and 0.018 Å, respectively. The HF/6-31G(d,p) method, however, provides a value for this bond which is 0.018 Å shorter than the experimentally determined one. This odd result demonstrates that the $\text{C}\equiv\text{N}$ bond length is not reasonably predicted by the theory, at least not by the ab initio methods we applied in this work.

It is perhaps of particular interest to indicate that the observed r_g mean values for the ring carbon–carbon distances in cyclopentane, MCCP and DCCP are 1.546(1) Å [28], 1.544(1) Å [18], and 1.555(3) Å (this work), respectively. Although the variation in the averaged $\text{C}-\text{C}$ bond distance is non-systematical, the lengthening of this bond in DCCP by 0.009 and 0.011 Å in comparison to cyclopentane and MCCP, respectively, indicates that the geminal substitution of cyclopentane by cyano groups leads to a general elongation of the ring $\text{C}-\text{C}$ bonds. Considering the distinct σ and π electron acceptor property of the cyano group this bond change appears to be minor. However, this

might be the consequence of competing effects like σ -charge withdrawal by the cyano group and ring strain. It remains to point out that the observed puckering amplitudes q of 0.427(15) Å [28], 0.426(28) Å [18], and 0.434(45) Å (this work) for cyclopentane, M CCP and D CCP, respectively, indicate that this parameter seems to be less sensitive to direct substitution on cyclopentane.

7. Summary and conclusions

In summary, from the presented experimental and ab initio results the following conclusions may be derived:

The electron diffraction data could be properly reproduced after the application of a dynamic pseudorotation model instead of a static model. To determine the pseudorotational potential function in more accurate fashion we had to account for the distinct dependency of the geometrical parameters as well as the vibrational amplitudes on the phase angle ϕ in D CCP. For a better justification of the pseudorotation model we found it more pertinent to include the dependency of the delocalized net charge distribution within the five-membered ring on the phase angle ϕ . Assuming similar puckering amplitudes for the C_s and C_2 symmetric forms and a regular pentagon we developed a charge distribution function which allows for the determination of the contribution of the delocalized net charges to a certain bond distance within the five-membered ring (Eqs. (2) and (3)). As to the best of our knowledge such kind of treatment of the pseudorotation motion in five-membered ring has not been employed before.

To calculate the reduced total molecular intensities within the frame of the pseudorotation model a total of 37 intermediary conformers in the range of $-135 \leq \phi \leq +45^\circ$ were incorporated into the structural analysis. Taking into account that large amplitude motions play an eminent role within D CCP (particularly the $C-C\equiv N$ groups) the experimental data could be best described by applying a r_α fit. For this purpose we adopted the necessary perpendicular vibrational amplitudes for the $r_a - r_\alpha$ corrections from the quadratic force field produced by the HF/6-31G** method.

From the present structural analysis of D CCP we found that the substitution of the hydrogen atom on C_1

in M CCP by an additional cyano group, in general, does not substantially affect the ring geometry. Perhaps the most intriguing result of this work is that evidence for the bond conjugation within the $C(CN)_2$ linkage could be derived from the NPA. In contrast to the MPA, based on the charge distribution provided by the NPA we could rationalize the moderate $\equiv C-C-C\equiv$ angle widening and the $C-C\equiv N$ angle bending by attractive and repulsive electrostatic interaction between the alternatively negatively and positively charged atoms within the $N\equiv C-C-C\equiv N$ fragment.

8. Supplementary data

Supplementary material has been deposited with the British Library Document Supply Centre as supplementary publication number sup 26686.

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