Atti Accademia Nazionale dei Lincei

Classe Scienze Fisiche Matematiche Naturali

Rendiconti

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An unusual Carbon-Carbon bond distance in substituted 1,6-methano[10]annulenes

Atti della Accademia Nazionale dei Lincei. Classe di Scienze Fisiche, Matematiche e Naturali. Rendiconti, Serie 8, Vol. **68** (1980), n.4, p. 307–309.

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<http://www.bdim.eu/item?id=RLINA_1980_8_68_4_307_0>

Atti della Accademia Nazionale dei Lincei. Classe di Scienze Fisiche, Matematiche e Naturali. Rendiconti, Accademia Nazionale dei Lincei, 1980.

SEZIONE II

(Fisica, chimica, geologia, paleontologia e mineralogia)

Strutturistica chimica. — *An unusual Carbon-Carbon bond distance in substituted 1,6-methano*[*10*]*annulenes.* Nota di RICCARDO BIANCHI, GABRIELE MOROSI e MASSIMO SIMONETTA, presentata (*) dal Socio M. SIMONETTA.

RIASSUNTO. — Il riesame dei dati raggi X e calcoli *ab initio* forniscono una nuova prova dell'esistenza di un legame C—C molto lungo in alcuni 1, 6–metano [10] annuleni sostituiti.

A quite unusual value around 1.8 Å for the C—C distance has been found in 11,11-dimethyltricyclo [4, 4, 1, $0^{1,6}$] undeca-2, 4, 7, 9-tetraene, hereafter referred to as DIM [1], and in 11-methyltricyclo [4, 4, 1, $0^{1,6}$] undeca-2,4-7, 9-tetraene-11-carbonitrile (hereafter CNME) [2].

The C (1)–C (6) distance in these compounds is too long to be considered a normal C—C bond and too short if compared to the distance of the corresponding non bonded atoms on 11,11-difluoro-1,6-methano[10]annulene [3] whose value is 2.27 Å.

The possibility of having in the crystal structure a statistical distribution of two isomers, the first closed and the second open, was excluded on the basis of the fact that the thermal factors B_{ij} should show large values, particularly along the C (1)—C (6) bond, while normal values were found [1, 2]. A lattice dynamical analysis [4] gave results consistent with these experimental data.

TABLE I

R *and* R_w *factors for selected* C (1)—C (6) *distances*

C (1)—C (6) (Å)	R	R_w
1.56	10.5	13.2
1.70	6.8	8.5
1.82	5.6	6.8
2.27	16.0	20.1

To further support the evidence of this very long C—C bond we report here the results of other refinements of X-ray data of CNME. To exclude that the least square refinement ended in a secondary minimum we constrained

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(*) Nella seduta del 12 aprile 1980.

the C (1)—C (6) distance to fixed values and optimized the geometry of CNME with respect to the other geometrical parameters, assuming TLS and *m* symmetry constraints for the two independent molecules in the asymmetric unit. In Table I we report the R and R_w factors for each imposed C (1)—C (6) distance.

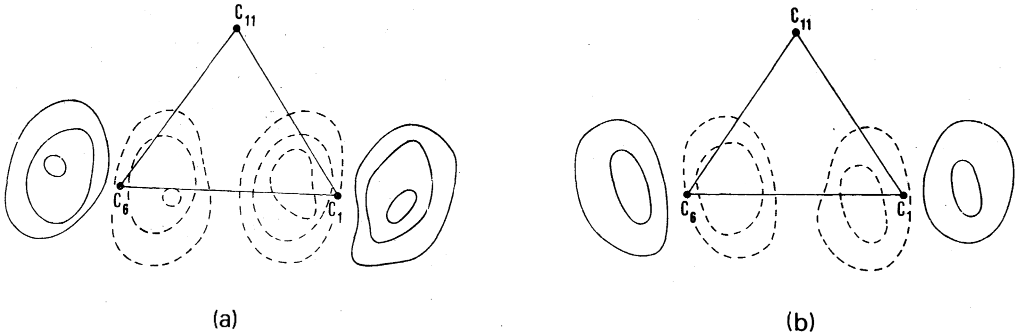

Fig. 1. – Difference map obtained for C (1)—C (6) = 1.56 Å. The plane corresponds to the cyclopropane ring of (*a*) molecule A, and (*b*) molecule B. Contour levels are at intervals of 0.30 e Å^{-3} (solid lines positive, dashed lines negative zero contours omitted).

The analysis of the results shown in the table shows that no secondary minima are present: the value C (1)—C (6) = 1.82 Å of the minimum corresponds to the average of the C (1)—C (6) distances found in the two independent molecules [2].

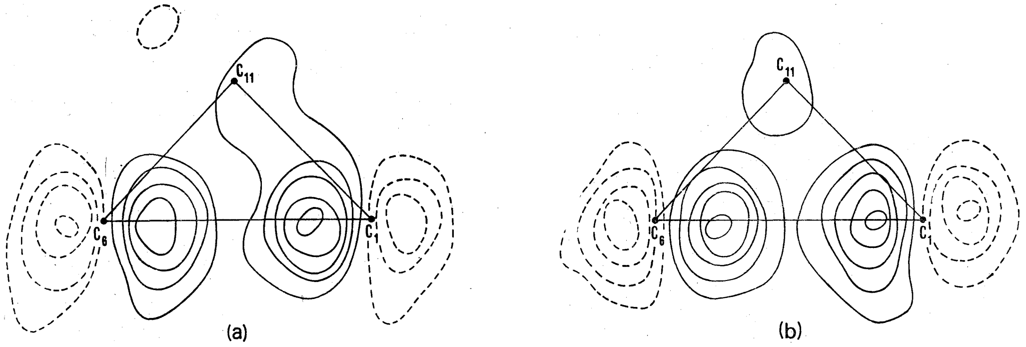

Fig. 2. – As Figure 1 for C (1)—C (6) = 2.27 Å.

In Figures 1 and 2 we show the final differences of electron density in the cyclopropane plane for refinements with C (1)—C (6) = 1.56 Å and 2.27 Å respectively. The minimum and maximum values of the residuals are between —1.36 and +1.62 e Å^{-3} for both cases, while for C (1)—C (6) = 1.82 Å the differences are between ± 0.22 e Å^{-3}.

Furthermore, we have done *ab initio* SCF calculations on 1,6-methano [10]annulene using a STO-3G basis set [5]. We have studied an open structure obtained by *mm 2* symmetrization of the geometry of 1,6-methano[10]annulene-2-carboxylic acid [6] and a structure with C (1)—C (6) = 1.82 Å obtained from CNME again by *mm 2* symmetrization. The open structure is more stable as expected on the basis of the experimental evidence for methano[10] annulenes [6, 7]. In Table II we report the values of atom-atom Mulliken's population analysis for ethane and the two annulene structures.

TABLE II

Mulliken's population analysis of C—C *bond*

C—C (Å)	C—C population
1.53	0.36
1.82	0.13
2.27	—0,01

We see that at 1.82 Å we have a weak bonding effect.

These results further support the existence of a bisnorcaradiene type structure for DIM and CNME with a very long C—C bond.

REFERENCES

[1] R. BIANCHI, G. MOROSI, A. MUGNOLI, and M. SIMONETTA (1973) – «*Acta Cryst.*», *B29*, 1196.

[2] R. BIANCHI, T. PILATI and M. SIMONETTA (1978) – «Acta Cryst.», *B 34*, 2157.

[3] T. PILATI and M. SIMONETTA (1976) – «Acta Cryst.», *B 32*, 1912.

[4] G. FILIPPINI, C. M. GRAMACCIOLI, M. SIMONETTA and G. B. SUFFRITTI (1974) – «Chem. Phys. Letters», *26*, 301.

[5] L. RADOM, W. A. LATHAN, W. J. HEHRE, and J. A. POPLE (1971) – «Journ. Amer. Chem. Soc.», *93*, 5339.

[6] M. DOBLER and J. D. DUNITZ (1965) – «Helv. Chim. Acta», *48*, 1429.

[7] E. VOGEL (1969) – «Pure Appl. Chem.», *20*, 237.