X-RAY ANALYSES AND MOLECULAR ORBITAL CALCULATIONS OF PYRIDINIUM DICYANOMETHYLIDES

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Abstract: Comparative studies have been described between X-ray analyses and molecular orbital calculations of *p*-substituted (H, Me, and Ac) pyridinium dicyanomethylides. Generally, *ab initio* calculations represent the geometry more well than semi-empirical methods.

The chemistry of cycloimmonium ylides has become extensive and numerous reactions have been reported.[1-3] The concept of *N*-ylides is introduced to heterocyclic chemistry using common printed representation: N^{+}-C^{-}. While this gives a sense of structure and charge separation the changes imply that the nitrogen and carbon are bound by a single covalent bond with an open valence on carbon. The experimentally derived solid phase N-C bond is found to have a bond length of 1.42 Å,[4] being smaller than that expected for a C_{sp2}-N_{sp2} bond. Few heterocyclic texts and reviews delve into the details of this intriguing structure.[1] Indeed, a theoretical treatment of this moiety is still lacking.[5] Previously, we have investigated substituent effects on ^{13}C and ^{15}N-NMR chemical shifts of the ylidic carbons and nitrogens of *p*-substituted pyridinium dicyanomethylides and bis(methoxycarbonyl)methylides.[6] Furthermore, sufficiently good correlations were found between the ^{13}C- and ^{15}N-NMR chemical shifts and the partial charges obtained by different computational methods (AM1, PM3, MNDO) of some *p*-substituted pyridinium dicyanomethylides[7] and bis(methoxycarbonyl)methylides.[8] Therefore, our research efforts led us to explore the best theoretical representation of several different aromatic *N*-ylides with the view to finding the computationally *inexpensive* method that could be reasonably expected to afford correct geometrical predictions. Thus we embarked to examine the case of pyridinium dicyanomethylides **1** as one of the simplest prototypical members of this series for which experimental data in the solid phase were and now are readily available. The classical CNDO calculations on this ylide **1a** with geometry determined by X-ray analysis[4] is reported to diverge.[5] In this paper, we describe briefly the results of X-ray crystal measurements of **1a-c** and the successful molecular orbital calculations as well as the data derived from both semi-empirical and *ab initio* molecular orbital calculations on the optimized geometry of **1a-c**.

X-ray crystal measurements of **1a-c** were also successful in our hands.[9] *Ab initio* and semi-empirical molecular orbital calculations were performed employing the commercially available softwares.[15, 16] The results are summarized in Tables 1~3 along with the previously obtained values (X ray) for **1a**.

First, we focussed our attention on the C-N bond length. Naturally, our bond length (1.424 Å) is almost exactly same as the previously obtained value of 1.420 Å, though the bond lengths of N1-C2, C2-C3, and C3-C4 were rather shorter than the previous ones. Previously it was found that substituents like CN, PhCO, and MeCO, cause deshielding of the ylidic carbons (C_7) while the ^{15}N chemical shifts are at higher fields. On the contrary, the alkyl-substituted pyridinium dicyanomethylides have more upfield ^{13}C chemical shifts for C_7 and more downfield ^{15}N chemical shifts for N_1 as compared with the unsubstituted pyridinium dicyanomethylide **1a**. Thus, when the substituents have a strong electron-withdrawing effect the contribution of resonance structures analogous to **1ab** becomes predominant and, in these pyridine *N*-ylides, the nitrogen-carbon bonds possess substantial double-bond character.[7,8] In agreement with this, **1b** having methyl group at 4-position had slightly longer bond length (1.427 Å) than that of the parent ylide **1a**, whereas **1c** having acetyl group had shorter bond length (1.415 Å) than **1a**. Inspection of Tables 1~3 clearly shows that semi-empirical calculations fail to give accurate

Table 1. Experimental and calculated bond lengths and bond angles of **1a**

Bond (Å)	X-ray (This work)	Previous work	STO-3G	STO-3G*	3-21G	3-21G*	4-31G	6-31G	6-31G*	6-31G**	6-311G	6-311G*	6-311G**	D95	MINDO/3	MNDO	AM1	PM3
N1-C2	1.359	1.370	1.382	1.382	1.354	1.354	1.352	1.355	1.356	1.346	1.354	1.344	1.344	1.359	1.386	1.398	1.381	1.386
C2-C3	1.368	1.390	1.376	1.376	1.371	1.371	1.371	1.375	1.374	1.373	1.374	1.372	1.372	1.381	1.398	1.401	1.396	1.390
C3-C4	1.377	1.390	1.389	1.389	1.383	1.383	1.382	1.386	1.383	1.382	1.385	1.382	1.382	1.393	1.386	1.404	1.395	1.392
C7-N1	1.424	1.420	1.421	1.421	1.428	1.426	1.424	1.427	1.422	1.422	1.426	1.422	1.422	1.432	1.363	1.392	1.381	1.382
C7-C8	1.396	1.390	1.417	1.400	1.383	1.388	1.389	1.394	1.401	1.401	1.394	1.399	1.399	1.400	1.443	1.411	1.410	1.409
C8-N10	1.153	1.130	1.162	1.165	1.148	1.148	1.151	1.156	1.144	1.144	1.151	1.138	1.138	1.162	1.163	1.165	1.165	1.163
Angle (°)	**X-ray (This work)**	**Previous work**	**STO-3G**	**STO-3G***	**3-21G**	**3-21G***	**4-31G**	**6-31G**	**6-31G***	**6-31G****	**6-311G**	**6-311G***	**6-311G****	**D95**	**MINDO/3**	**MNDO**	**AM1**	**PM3**
N1-C2 C3	120.8	119.3	121.4	121.4	121.4	121.4	121.4	121.4	121.7	121.6	121.4	121.7	121.7	121.4	121.1	121.6	121.7	121.6
C2-C3-C4	120.4	120.3	120.6	120.6	120.1	120.1	120.2	120.2	120.0	120.0	120.2	120.0	120.0	120.1	120.3	120.4	120.3	120.3
C3-C4-C5	118.3	118.6	118.1	118.1	118.1	118.1	118.0	117.9	117.8	117.8	117.9	117.8	117.7	117.9	116.1	118.2	118.2	118.3
C6-N1-C2	119.2	120.2	117.8	117.8	118.9	118.9	118.9	118.9	118.8	118.9	118.9	120.6	118.9	119.0	115.0	117.9	117.9	117.9
C2-N1-C7	120.4	119.2	120.1	121.1	120.6	120.6	120.6	120.5	120.6	120.6	120.6	118.6	120.6	120.5	122.4	120.1	120.6	121.1
N1-C7-C8	120.0	120.1	118.6	118.6	118.3	118.4	118.4	118.7	118.7	118.6	118.5	118.7	118.7	118.8	121.0	121.2	121.2	121.4
C7-C8-N10	177.9	180.0	180.0	179.6	179.6	179.6	178.0	177.4	177.4	177.7	178.3	177.4	177.6	179.1	-	-	-	-
C8-C7-C9	120.0	119.2	122.7	121.7	123.5	123.5	123.2	122.7	122.7	122.3	123.1	122.7	122.7	122.4	116.1	117.7	117.7	117.1

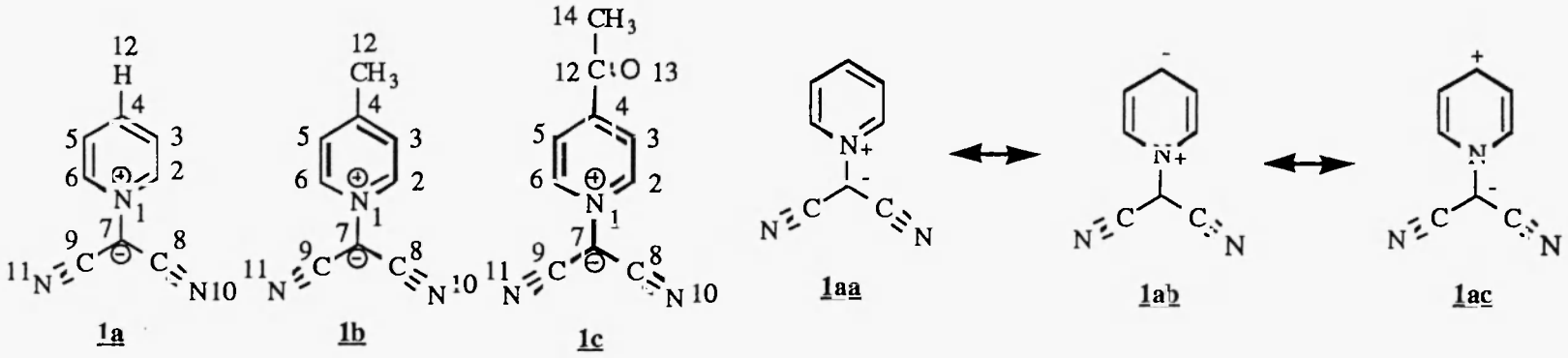

Table 2. Experimental and calculated bond lengths and bond angles of **1b**

Bond (Å)	X-ray	STO-3G	STO-3G*	3-21G	3-21G*	4-31G	6-31G	6-31G*	6-31G**	6-311G	6-311G*	6-311G**	D95	MINDO/3	MNDO	AM1	PM3
N1-C2	1.354	1.378	1.378	1.350	1.350	1.353	1.350	1.343	1.341	1.349	1.340	1.340	1.354	1.384	1.398	1.381	1.387
C2-C3	1.364	1.378	1.376	1.371	1.371	1.370	1.375	1.369	1.374	1.374	1.374	1.374	1.382	1.396	1.398	1.395	1.388
C3-C4	1.384	1.392	1.392	1.385	1.385	1.384	1.389	1.387	1.386	1.389	1.385	1.385	1.396	1.422	1.415	1.399	1.395
C4-C5	1.384	1.397	1.397	1.390	1.390	1.387	1.393	1.385	1.391	1.393	1.390	1.391	1.400	1.421	1.411	1.401	1.397
C5-C6	1.364	1.372	1.372	1.357	1.387	1.366	1.372	1.369	1.369	1.370	1.368	1.368	1.378	1.394	1.398	1.395	1.388
C6-N1	1.354	1.381	1.382	1.354	1.354	1.358	1.354	1.341	1.346	1.353	1.345	1.345	1.358	1.384	1.362	1.382	1.388
C7-N1	1.427	1.425	1.425	1.424	1.434	1.408	1.432	1.427	1.427	1.433	1.428	1.428	1.439	1.362	1.398	1.383	1.382
C7-C8	1.390	1.415	1.415	1.387	1.387	1.392	1.392	1.400	1.400	1.393	1.398	1.398	1.399	1.444	1.412	1.410	1.409
C7-C9	1.393	1.415	1.415	1.387	1.387	1.392	1.392	1.400	1.400	1.393	1.398	1.398	1.399	1.444	1.412	1.410	1.409
C8-N10	1.146	1.167	1.162	1.148	1.148	1.150	1.157	1.144	1.144	1.152	1.138	1.138	1.162	1.163	1.165	1.165	1.163
C9-N11	1.149	1.167	1.162	1.148	1.148	1.150	1.157	1.144	1.144	1.152	1.138	1.138	1.162	1.163	1.165	1.165	1.163
C4-C12	1.509	1.523	1.523	1.511	1.511	1.489	1.504	1.503	1.505	1.502	1.504	1.505	1.508	1.487	1.504	1.478	1.483
Angle (°)	X-ray	STO-3G	STO-3G*	3-21G	3-21G*	4-31G	6-31G	6-31G*	6-31G**	6-311G	6-311G*	6-311G**	D95	MINDO/3	MNDO	AM1	PM3
N1-C2-C3	121.1	121.6	121.6	121.6	121.6	121.6	121.6	121.8	121.8	121.6	121.9	121.9	121.6	124.2	121.9	121.7	121.3
C2-C3-C4	121.6	121.3	121.3	120.9	120.9	121.0	121.1	121.0	120.9	121.1	120.9	120.9	121.0	124.9	121.3	120.7	120.6
C3-C4-C5	116.2	116.7	116.7	116.7	116.7	116.3	116.3	116.1	116.1	116.2	116.1	116.1	116.3	112.0	116.5	117.5	118.2
C4-C5-C6	121.6	121.4	121.4	120.9	120.9	121.1	121.1	121.0	121.0	121.1	120.9	121.1	121.0	121.6	121.6	120.7	120.6
C5-C6-N1	121.0	121.5	121.5	121.5	121.5	121.5	121.5	121.8	121.8	121.6	121.9	121.6	121.6	124.2	121.9	121.6	121.3
C6-N1-C2	113.6	117.5	117.5	118.5	118.5	116.5	118.5	118.4	118.4	118.5	118.3	118.1	118.6	113.2	116.9	117.9	118.1
C2-N1-C7	121.0	121.3	121.3	120.8	120.8	120.8	120.8	120.9	120.9	120.9	121.0	120.9	120.8	123.1	121.4	120.1	120.8
C6-N1-C7	120.5	121.2	121.2	120.7	120.7	120.7	120.7	120.7	120.7	120.7	120.7	120.7	120.6	123.7	121.7	122.0	121.7
N1-C7-C8	119.7	118.5	118.5	118.1	118.1	118.3	118.3	118.6	118.6	118.3	118.6	120.7	118.7	121.8	121.8	121.2	121.4
N1-C7-C9	119.0	118.5	118.5	118.1	118.1	118.2	118.3	118.5	118.5	118.2	118.5	118.2	118.6	121.6	121.4	121.2	121.4
C8-C7-C9	121.2	123.0	123.0	123.8	123.8	123.5	123.5	123.8	123.0	123.4	123.0	123.0	122.6	113.8	117.3	117.7	117.2
C7-C8-N10	179.4	179.9	179.9	179.5	179.5	177.9	177.8	177.3	177.3	178.2	177.5	177.5	179.0	-	-	-	-
C7-C9-N11	179.3	179.9	179.9	179.5	179.5	177.8	177.7	177.2	177.2	178.1	177.5	178.1	178.9	-	-	-	-
C3-C4-C12	122.4	122.1	122.1	122.3	122.2	122.1	122.3	122.4	122.4	122.3	122.5	122.3	122.3	124.2	122.2	121.7	121.4
C5-C4-C12	121.5	121.2	121.2	121.1	121.1	121.4	121.5	121.5	121.5	121.5	121.4	121.5	121.4	123.8	121.1	120.8	120.4

Table 3. Experimental and calculated bond lengths and bond angles of **1c**

Bond (Å)	X-ray	STO-3G	STO-3G*	3-21G	3-21G*	4-31G	6-31G	6-31G*	6-31G**	6 311G	6-311G*	6-311G**	D95	MINDO/3	MNDO	AM1	PM3
N1-C2	1.354	1.378	1.383	1.356	1.356	1.353	1.356	1.349	1.346	1.355	1.344	1.344	1.360	1.391	1.398	1.385	1.356
C2-C3	1.362	1.394	1.394	1.383	1.383	1.384	1.374	1.374	1.374	1.373	1.374	1.373	1.381	1.389	1.398	1.394	1.374
C3-C4	1.393	1.394	1.394	1.383	1.383	1.384	1.388	1.385	1.385	1.387	1.384	1.384	1.393	1.426	1.414	1.399	1.383
C4-C5	1.375	1.397	1.397	1.386	1.383	1.387	1.391	1.389	1.389	1.391	1.388	1.388	1.398	1.430	1.416	1.404	1.386
C5-C6	1.374	1.371	1.371	1.365	1.365	1.366	1.370	1.369	1.368	1.368	1.367	1.367	1.376	1.390	1.400	1.392	1.365
C6-N1	1.366	1.386	1.386	1.361	1.361	1.358	1.361	1.352	1.352	1.360	1.351	1.351	1.368	1.391	1.398	1.385	1.361
C7-N1	1.415	1.414	1.414	1.411	1.411	1.408	1.411	1.408	1.408	1.411	1.409	1.409	1.416	1.350	1.386	1.375	1.411
C7-C8	1.388	1.419	1.419	1.391	1.391	1.392	1.397	1.404	1.404	1.397	1.402	1.402	1.403	1.448	1.414	1.413	1.391
C7-C9	1.384	1.419	1.419	1.391	1.391	1.392	1.397	1.404	1.404	1.397	1.402	1.402	1.403	1.448	1.414	1.413	1.391
C8-N10	1.140	1.161	1.161	1.147	1.147	1.150	1.155	1.143	1.143	1.150	1.137	1.137	1.160	1.162	1.164	1.164	1.147
C9-N11	1.176	1.161	1.161	1.147	1.147	1.150	1.155	1.143	1.143	1.150	1.137	1.137	1.160	1.162	1.164	1.164	1.147
C4-C12	1.516	1.524	1.524	1.495	1.495	1.489	1.492	1.506	1.506	1.491	1.508	1.508	1.499	1.502	1.506	-	1.495
C12-C14	1.494	1.540	1.540	1.509	1.509	1.501	1.502	1.506	1.509	1.499	1.509	1.509	1.510	-	1.412	1.492	1.509
C12-O13	1.215	1.223	1.223	1.213	1.213	1.215	1.202	1.192	1.192	1.218	1.186	1.186	1.224	1.212	1.219	1.492	1.213
Angle (°)	**X-ray**	**STO-3G**	**STO-3G***	**3-21G**	**3-21G***	**4-31G**	**6-31G**	**6-31G***	**6-31G****	**6-311G**	**6-311G***	**6-311G****	**D95**	**MINDO/3**	**MNDO**	**AM1**	**PM3**
N1-C2-C3	121.2	121.7	121.6	121.5	121.5	121.5	121.5	121.7	121.7	121.5	121.8	121.7	121.5	123.0	122.0	121.7	121.4
C2-C3-C4	121.0	121.1	121.1	120.4	120.4	120.7	120.7	120.6	120.6	120.7	120.5	120.5	120.6	124.9	122.0	121.6	120.8
C3-C4-C5	117.3	117.0	117.0	117.5	117.5	117.1	117.0	116.9	116.9	117.0	116.9	116.9	117.1	110.5	115.3	117.7	117.8
C4-C5-C6	121.0	121.5	121.5	120.8	120.8	120.8	120.8	120.7	120.6	120.8	120.6	120.6	120.7	124.0	122.4	120.7	120.8
C5-C6-N1	121.4	121.3	121.3	121.2	121.2	121.4	121.4	120.6	121.6	121.4	121.7	121.6	121.4	123.0	122.0	121.7	121.4
C6-N1-C2	118.5	117.6	117.6	118.6	118.6	118.5	118.6	118.6	118.7	118.5	118.5	118.6	118.6	123.0	121.5	121.1	121.1
C2-N1-C7	120.6	121.2	121.2	120.8	120.8	120.8	120.7	120.8	120.7	120.8	120.8	120.8	120.7	122.4	121.3	121.4	120.6
C6-N1-C7	120.9	121.2	121.2	120.7	120.7	120.7	120.7	120.7	120.7	120.7	120.7	120.7	120.6	122.4	121.3	121.4	120.5
N1-C7-C8	119.3	118.8	118.9	118.7	118.7	118.8	118.8	119.0	119.0	118.9	119.0	119.0	119.2	122.3	121.3	121.4	118.6
N1-C7-C9	119.3	118.8	118.8	118.6	118.6	118.6	118.6	118.8	118.8	118.7	118.8	118.8	119.0	122.3	121.3	121.4	118.6
C8-C7-C9	121.1	122.4	122.4	122.8	122.8	122.6	122.5	122.2	122.2	122.5	122.2	122.2	121.8	115.5	117.4	117.2	116.8
C7-C8-N10	177.7	179.9	179.9	179.9	179.9	178.5	178.3	177.9	177.8	178.7	178.0	178.0	179.4	-	-	-	-
C7-C9-N11	177.6	180.0	180.0	179.7	179.7	178.1	177.9	177.4	177.4	178.3	177.6	177.6	179.1	-	-	-	-
C3-C4-C12	122.2	124.0	124.0	122.8	122.8	123.7	123.6	124.1	124.1	123.6	124.1	124.1	123.5	126.2	123.7	-	-
C5-C4-C12	120.5	119.1	119.0	118.0	118.0	119.2	119.3	119.1	119.0	119.4	119.0	119.0	119.4	123.3	121.0	-	-
C4-C12-O13	119.3	119.9	119.3	119.4	119.4	119.2	119.1	119.2	119.1	119.6	119.2	119.1	119.1	123.3	120.2	-	-
O13-C12-C14	122.7	122.2	122.2	122.8	122.8	121.4	121.2	121.9	121.9	121.2	122.1	122.1	121.4	-	-	120.8	121.2
C4-C12-C14	117.9	117.9	117.9	117.9	117.9	119.4	119.7	118.9	119.0	119.0	118.8	118.8	119.6	-	-	-	-

representations of the ylidic moiety (N^+-C^-, C7-N1) of pyridinium dicyanomethylides **1**, while, in general, *ab initio* calculations represent more well this bond length, even if we use lower levels of *ab initio* calculations such as STO-3G. In the case of **1c**, PM3 method (1.411Å) reproduces this moiety as well as *ab initio* methods do.

Next, the geometry including bond lengths and bond angles was considered. In the case of the parent ylide **1a**, the 3-21G, 4-31G, 6-31G, and D-95 methods (standard deviations from X-ray data=0.005) afforded best reproduction of bond lengths, while the 4-31G method gave the smallest standard deviation (0.9) from X-ray data with respect to the bond angles. Thus, the 4-31G method seems to be best for reproduction of total geometry of **1a**. The analogous analyses regarding **1b** showed that the 3-21G method had smaller standard deviations of 0.003 for bond lengths and 0.8 for bond angles, though the D-95 method gave more smaller standard deviation (0.5) for bond angles but larger one (0.006) for bond lengths. In contrast with **1a** and **1b**, 4-acetylpyridinium dicyanomethylide **1c** seems to need higher levels of *ab initio* calculations to represent the total geometry. Indeed, the smallest standard deviations (0.011, 0.012) for bond lengths were obtained by D95 and 6-31G respectively, while the deviations (0.7, 0.7, 0.8) for bond angles were obtained by 6-31IG*, 6-311G**, and 6-31G. Thus, the 6-31 level of calculation is presumably appropriate for reasonable representation of the geometry of **1c**.

In conclusion, semi-empirically derived values (MNDO, AM 1, PM3) show poor agreement with solid phase derived bond lengths and angles, whereas *ab initio* methods seems to provide better agreement with experiment.

Further work on comparative studies of related ylides between X-ray data and molecular orbital calculations specifically including Density Functional Theory Approach (DFT) Method is in progress and will be subjects of further communications.

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References

(1) I. Zugravescu and M. Petrovanu, *N-Ylide Chemistry*, McGraw Hill International, New York (1976)
(2) G. Surpateanu, J. P. Catteau, P. Karafiloglu and A. Lablanche, *Tetrahedron*, 32, 2647 (1976)
(3) K. Matsumoto, H. Katsura,T. Uchida, K. Aoyama and T. Machiguchi, *J. Chem. Soc., Perkin Trans. 1*, 2599 (1996) and previous work from our laboratory.
(4) C. Buss, R. Desiderato and R. L. Sass, *J. Am. Chem. Soc.*, 86, 3157(1964)
(5) Ref. 2, page 2649
(6) K. Matsumoto, T. Uchida and C. Uno, *Heterocycles*, 19, 1849 (1982); K. Matsumoto, T. Uchida, Y. Ikemi, H. Fujita, K. Aoyama and M. Asahi, *Heterocycles*, 24, 339(1986)
b) K. Matsumoto, T. Uchida, K. Aoyama, T. Tanaka and M. Asahi, *Chem. Express*, 1, 419 (1986); 1, 423 (1986)
(7) K. Matsumoto, H. Katsura, T. Uchida, K. Aoyama and T. Machiguchi, *Heterocycles*, 45, 2443 (1997)
(8) K. Matsumoto, M. Ciobanu, K. Aoyama and T. Uchida, *Heterocyclic Communications*, 3, 499 (1997)
(9) Data were collected at T=20°C on a Rigaku AFC5S diffractometer; **1a**: $C_8H_5N_3$, M=143.15, yellow prism, dimensions 0.100 x 0.600 x 0.540 mm, monoclinic, space group = $P2_1/m$, a = 3.881(5)Å , b = 12.542(5)Å, c =7.183(5)Å, β =94.81(1)°, U=348.4 (5)Å^3, Z= 2, Dc=1.364gcm^{-3}, F(000)=148. Mo-Kα radiation (λ=0.71069Å) μ=0.082 mm^{-1}, ω-2Θ scan mode with ω scan width=1.31 + 0.30tanθ, ω scan speed 32.0 deg min^{-1}, 951 reflections were collected in the range 6.0<2θ<55.0 and 835 unique reflections (R_{int}=0.016) were used in the refinement. The structure was solved by direct methods[10] using full-matrix least squares on *F* for all non-hydrogen atoms using Lorenz polarization and absorption corrections to give R=0.043, and Rw=0.052 for 588 independent observed reflections with I >2.00σ(I) and 67 variables for 2θmax=55.0°. The final difference map maximum and minimum were 0.20 and -0.18 eÅ^{-3}, respectively. **1b**: $C_9H_7N_3$, M=157.17, yellow prism, dimensions 0.280 x 0.760 x1.000 mm, triclinic, space group=$P\bar{1}$ (#2), a=7.520(1)Å , b = 8.915(1)Å, c=7.300(1)Å, α =106.86(1)°, β =115.52(1)°, γ =75.58(1)°, U=418.3 (1)Å^3, Z=2, Dc=1.248gcm^{-3}, F(000)=164. Mo-Kα radiation (λ=0.71069Å) μ=0.074 mm^{-1}, ω-2Θ scan mode with ω scan width=1.52 + 0.30tanθ, ω scan speed 32.0 deg min^{-1}, 2066 reflections were collected in the range 5.0<2θ<55.0 and 1917 unique reflections (R_{int}=0.024) were used in the refinement. The structure was solved by direct

methods using full-matrix least squares on *F* for all non-hydrogen atoms using Lorenz polarization and absorption corrections to give R=0.046, and Rw=0.055 for 1358 independent observed reflections with I >2.00σ(I) and 156 variables for 2θmax=55.0°. The final difference map maximum and minimum were 0.18 and -0.18 e Å^{-3}, respectively. **1c**: $C_{10}H_7N_3O$, M=185.18, dark prism, dimensions 0.080 x 0.320 x 0.840 mm, monoclinic, space group=$P2_1/c$(#14), a=10.169(2) Å, b=8.968(1) Å, c=10.602(2) Å, β=115.52(1)°, U=418.3 (1) Å^3, Z=4, Dc=1.356gcm^{-3}, F(000)=384. Mo-Kα radiation (λ=0.71069 Å) μ=0.082 mm^{-1}, ω-2Θ scan mode with ω scan width=1.73 + 0.90tanθ, ω scan speed 32.0 deg min^{-1}. 2490 reflections were collected in the range 6.0<2θ<55.0 and 2225 unique reflections (R_{int}=0.458) were used in the refinement. The structure was solved by direct methods[10] using full-matrix least squares on *F* for all non-hydrogen atoms using Lorenz polarization and absorption corrections to give R=0.060, and Rw=0.058 for 894 independent observed reflections with I >2.00σ(I) and 156 variables for 2θmax=55.0°. The final difference map maximum and minimum were 0.24 and -0.25 e Å^{-3}, respectively. The atomic scattering factors for all atoms and the anomalous dispersion correction factors for atoms other than hydrogen were taken from the literature.[11-13] All caculations were performed using TEXAN[14] crystallographic software package of Molecular Structure Corporation

(10) MITHRIL: C. J. Gilmore, *J. Appl. Cryst.*, 17, 42 (1984); DIRDIF: P. T. Beurskens, Technical Report 1984/1, Crystallography Laboratory, Toernooiveld, 6525 Ed Nijmegen, Netherlands

(11) D. T. Cromer and J. T. Weber, International Tables for X-ray Crystallography, Vol. IV, The Kynoch Press, Birmingham, UK, 1974, Table 2.2A

(12) J. A. Ibers and W. C. Hamilton, *Acta Crystallogr.*, 17, 781 (1964)

(13) D. T. Cromer, International Tables for X-ray Crystallography, Vol.IV, The Kynoch, Birmingham, UK, 1974, Table 2.3.1

(14) TEXRAY Structure Analysis Package, Molecular Structure Corporation, 1985

(15) Semi-empirical calculations were performed using CAChe systems (Version 3.7, CAChe Scientific, Oxford Molecular Group; MINDO/3: R. C. Bingham, M. J. S. Dewar, and D. H. Lo, *J. Am. Chem. Soc.*, 97, 1294 (1975); MNDO: M. J. S. Dewar and W. J. Thiel, 99, 4899 (1977); AMI: M. J. S. Dewar, E. G. Zoebisch, E. F. Hearly, and J. J. P. Stewart, *J. Am. Chem. Soc.*, 107, 3902 (1985); PM3: J. J. P. Stewart, *J. Comp. Chem.*, 10, 209 (1989) and references cited

(16) *Ab initio* calculations were performed by IBM R6000 computer using Mulliken 2.0 package (Version 2.0, IBM Corporation). STO-3G : W. J. Hehre, R. F. Stewart and J. A. Pople, *J. Chem. Phys.*, 51, 2657 (1969); W. J. Hehre, R. Ditchfield, R. F. Stewart and J. A. Pople, *J. Chem. Phys.*, 52, 2769 (1970); W. J. Pietro, B. A. Levi, W. J. Hehre and R. F. Stewart, *Inorg. Chem.*, 1980, 19, 2225 (1980); W. J. Pietro and W. J. Hehre, *J. Comput. Chem.*, 4, 241 (1983). STO-3G* : J. B. Collins, P. v. R. Schleyer, J. S. Binkley and J. A. Pople, *J. Chem. Phys.*, 64, 5142 (1976). 3-21G : W. J. Pietro, M. M. Francl, W. J. Hehre, D. J. DeFrees, J. A. Pople and J. S. Binkley, *J. Am. Chem. Soc.*, 104, 5039 (1982). 3-21G* : W. J. Pietro, M. M. Francl, W. J. Hehre, D. J. DeFrees, J. A. Pople and J. S. Binkley, *J. Am. Chem. Soc.*, 104, 5039 (1982). 4-31G : R. Ditchfield, W. J. Hehre and J. A. Pople, *J. Chem. Phys.*, 54, 724 (1971); W. J. Hehre and J. A. Pople, *J. Chem. Phys.*, 56, 4233 (1972); J. D. Kill and J. A. Pople, *J. Chem. Phys.*, 62, 2921 (1975); W. J. Hehre and W. A. Lathan, *J. Chem. Phys.*, 56, 5255 (1972). 6-31G : W. J. Hehre, R. Ditchfield and J. A. Pople, *J. Chem. Phys.*, 56, 2257 (1972); J. S. Binkley, J. A. Pople, and W. J.Hehre, *J. Chem. Phys.*, 66, 879 (1977); M. M.Francl, W. J. Pietro, W. J. Hehre, J. S. Binkley, D. J. DeFrees and J. A. Pople, *J. Chem. Phys.*, 77, 3654 (1982). 6-31G* : P. C. Hariharan and J. A. Pople, *Chem. Phys. Lett.*, 66, 217 (1972); M. M. Francl, W. J. Pietro, W. J. Hehre, J. S. Binkley, D. J. DeFrees and J. A. Pople, *J. Chem. Phys.*, 77, 3654 (1982). 6-31G** : W. J. Hehre, L. Radom, P. v. R.Schleyer and J. A. Pople, *Ab initio Molecular Orbital Theory*, John Wiley & Sons, New York, 1986, p.82. 6-311G : R. Krishnan, M. J. Frisch and J. A. Pople, *J. Chem. Phys.*, 72, 4244 (1980). 6-311G* : R. Krishnan, M. J. Frisch and J. A. Pople, *J. Chem .Phys.*, 72, 4244 (1980). 6-311G** : R. Krishnan, M. J. Frisch and J. A. Pople, *J. Chem. Phys.*, 72, 4244 (1980). D95 : T. H. Dunning, *J. Chem. Phys.*, 55, 2823 (1970); T. H. Dunning and P. J. Hay, *Gaussian Basic Sets for Molecular Calculations in Method of Electronic Structure Theory*, ed. H. F. Schaefer III, Plenum Press, New York, 1977. D95* : T. H. Dunning, *J. Chem. Phys.*, 55, 3958 (1971); E. Magnusson and H. F. Schaefer III, *J. Chem. Phys.*, 83, 5721 (1985)

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