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Comparative X-ray Diffraction Studies and Molecular Orbital Calculations on Diazinium Dicyanomethylides

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Comparative studies have been described between X-ray analyses (1a: *Pnma* (No. 62), $a = 9.069(4)$ Å, $b = 6.411(4)$ Å, $c = 12.299(3)$ Å, $U = 715.1(5)$ Å^3, $Z = 4$, $Dc = 1.3339\,\mathrm{gcm}^{-3}$, $R = 0.052$, and $R_w = 0.066$ for 599 independent observed reflections. 1b: $P2_1/m$ (No. 11), $a = 3.824(5)$ Å, $b = 12.593(3)$ Å, $c = 6.685(3)$ Å, $= 91.80(6)°$, $U = 321.8(4)$ Å^3, $Z = 2$, $Dc = 1.487\,\mathrm{gcm}^{-3}$, $R = 0.052$, and $R_w = 0.063$ for 599 independent observed reflections) and molecular orbital calculations of pyridazinium (1a) and pyrazinium (1b) dicyanomethylides. Generally, *ab initio* calculations reproduce the geometry better than semi-empirical methods.

Keywords: X-ray diffraction; Stable ylide; MO calculations; Cycloimmonium ylide

INTRODUCTION

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 the 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 for the parent pyridinium dicyanomethylide [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 [1,2]. Indeed, a theoretical treatment of this moiety is still lacking, although Vergoten and Surpateanu *et al.*, have reported a comparative X-ray diffraction study and *ab initio* MO calculations on amidocyanopyridinium methylide [5]. Previously, we have investigated substituent effects on ^{13}C and ^{15}N-NMR chemical shifts of the ylidic carbons and nitrogens of 4-substituted pyridinium dicyanomethylides and bis(methoxycarbonyl)methylides [6]. Furthermore,

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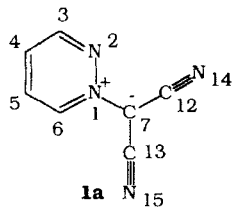
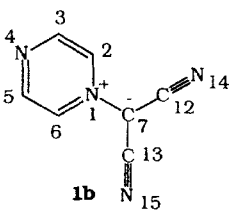
sufficiently good correlations were found between the ^{13}C- and ^{15}N-NMR chemical shifts and the partial charges obtained by different computational methods (AM1, PM3, MNDO) of some *p*-substituted pyridinium dicyanomethylides [7] and bis(methoxycarbonyl)methylides [8]. Therefore, our research efforts led us to explore the best theoretical representation of several different aromatic *N*-ylides with a view to finding the computationally *inexpensive* method that could be reasonably expected to afford correct geometrical predictions. Recently, we briefly reported comparative studies between X-ray analyses and molecular orbital calculations of 4-substituted (H, Me, and Ac) pyridinium dicyanomethylides [9]. Generally, *ab initio* calculations represent the geometry better than semi-empirical methods. In this paper, we briefly describe comparative studies between the results of X-ray crystal measurements of pyridazinium and pyrazinium dicyanomethylides **1a**, **b** and the data derived from both semi-empirical and *ab initio* molecular orbital calculations on the optimized geometry of **1a**, **b**.



1a



1b

RESULTS AND DISCUSSION

Pyridazinium ylide **1a** and pyrazinium ylide **1b** were prepared according to the method of Linn *et al.* [10] However, unfortunately, attempts to prepare the third isomer, pyrimidinium dicyanomethylide, by this method gave only a very low yield of the product, from which no single crystal was able to be isolated in our hands.

X-ray crystal measurements of **1a**, **b** were performed as before [9, 11], and their molecular and crystal structures are depicted in Figure 1. It is worth noting in passing that both **1a** and **1b** are arranged in a head-to-tail fashion presumably due to dipole–dipole interaction. *Ab initio* and semi-empirical molecular orbital calculations were performed employing commercially available software [12, 13]. The results are summarized in Tables I–IV

First, we focused our attention on the C–N bond length. 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. Thus, when the substituents have a strong electron-withdrawing effect the contribution of resonance structures analogous to **B** becomes predominant and, in these pyridinium *N*-ylides, the nitrogen–carbon bonds possess substantial double-bond character [7, 8]. In agreement with this, 4-methylpyridinium dicyanomethylide having a methyl group at the 4-position had slightly longer bond length (1.427 Å) than that of the parent pyridinium dicyanomethylide, whereas 4-acetylpyridinium dicyanomethylide having an acetyl group had shorter bond length (1.415 Å) than the parent one. The diazinium dicynomethylides **1a**, **1b** could be regarded, in a rough approximation, as the corresponding nitropyridinium dicynomethylide as pyridine is roughly regarded as nitrobenzene. Thus, the ylides **1a**, **1b** had the shorter bond lengths (1.403 and 1.404 Å). As summarized in Scheme 1, the 6-31G** level calculations rather accurately reproduce the observed C–N bond lengths of various heteroaromatic dicyanomethylides. Regarding the C–N bond length (Tab. I), either an STO-3G or an STO-3G* level of calculations and even semi-empirical calculations like MNDO and

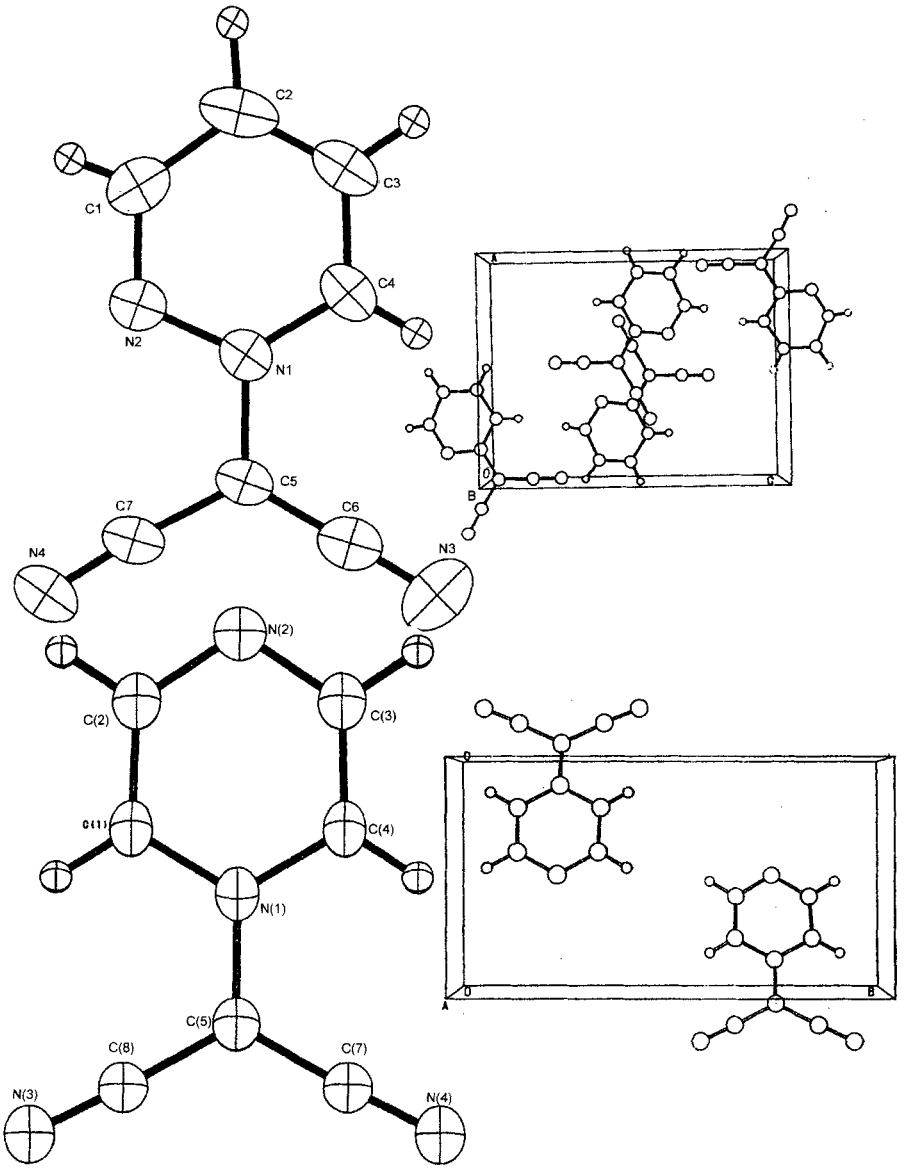


FIGURE 1 Molecular and crystal structure of **1a** and **1b**, above: **1a**, below: **1b**.

AM1 best represent the C–N bond length of **1a**, and the calculated values of the C–N bond ($N^+ - C^-$, C7 – N1) length were not improved by employing higher levels of *ab initio* calculations. In contrast, an inspection of Table III clearly shows that semi-empirical calculations fail to give accurate representations of the ylidic moiety of pyrazinium dicyanomethylides **1b**, while, in general, *ab initio* calculations (STO-3G*, D95) better represent this bond length.

Next, the geometry, including bond lengths and bond angles, was considered. The results are summarized in Table V. In the case of the ylide **1a**, the 4-31G, 6-31G and 6-311G methods (standard deviations from X-ray data = 1.21, 1.20) afforded moderate reproduction of bond

TABLE I Experimental and calculated bond lengths (Å) of pyridazinium dicyanomethylide **1a**

Bond	X-ray	STO-3G Cal.	STO-3G Dif.	STO-3G % of Dif.	STO-3G* Cal.	STO-3G* Dif.	STO-3G* % of dif.	3-21G Cal.	3-21G Dif.	3-21G % of dif.	3-21G* Cal.	3-21G* Dif.	3-21G* % of dif.	4-31G Cal.	4-31G Dif.	4-31G % of dif.	6-31G Cal.	6-31G Dif.	6-31G % of dif.
N1–N2	1.334	1.394	0.060	4.50	1.394	0.060	4.50	1.364	0.030	2.25	1.364	0.030	2.25	1.335	0.001	0.07	1.334	0.000	0.00
N1–C6	1.344	1.387	−0.043	−3.20	1.387	−0.043	−3.20	1.352	−0.008	−0.60	1.352	−0.008	−0.60	1.352	−0.008	−0.60	1.355	−0.011	−0.82
N1–C7	1.404	1.389	0.015	1.07	1.389	0.015	1.07	1.371	0.033	2.35	1.371	0.033	2.35	1.375	0.029	2.07	1.379	0.025	1.78
N2–C3	1.327	1.347	−0.020	−1.51	1.347	−0.020	−1.51	1.315	0.012	0.90	1.315	0.012	0.90	1.317	0.010	0.75	1.320	0.007	0.53
C3–C4	1.379	1.391	−0.012	−0.87	1.391	−0.012	−0.87	1.386	−0.007	−0.51	1.386	−0.007	−0.51	1.382	−0.003	−0.22	1.386	−0.007	−0.51
C4–C5	1.343	1.386	−0.043	−3.20	1.386	−0.043	−3.20	1.375	−0.032	−2.38	1.375	−0.032	−2.38	1.378	−0.035	−2.61	1.382	−0.039	−2.90
C5–C6	1.383	1.374	0.009	0.65	1.374	0.009	0.65	1.375	0.008	0.58	1.375	0.008	0.58	1.373	0.010	0.72	1.377	0.006	0.43
C7–C12	1.383	1.425	−0.042	−3.04	1.425	−0.042	−3.04	1.395	−0.012	−0.87	1.395	−0.012	−0.87	1.396	−0.013	−0.94	1.400	−0.017	−1.23
C7–C13	1.404	1.428	−0.024	−1.71	1.428	0.024	1.71	1.397	0.007	0.50	1.397	0.007	0.50	1.399	0.005	0.36	1.403	0.001	0.07
C12–N14	1.141	1.161	−0.020	−1.75	1.161	−0.020	−1.75	1.145	0.004	0.35	1.145	−0.004	−0.35	1.149	−0.008	−0.70	1.154	−0.013	−1.14
C13–N15	1.153	1.160	−0.007	−0.61	1.160	−0.007	−0.61	1.143	0.010	0.87	1.143	0.010	0.87	1.146	0.007	0.61	1.151	0.002	0.17
		SD =	0.023	1.71	SD =	0.023	1.71	SD =	0.019	1.40	SD =	0.019	1.40	SD =	0.016	1.20	SD =	0.016	1.21
		6-31G*			6-31G**			6-311G			6-311G*			6-311G**			D95		
Atom																			
N1–N2	1.334	1.314	0.020	1.50	1.314	0.020	1.50	1.335	−0.001	−0.07	1.312	0.022	1.65	1.312	0.022	1.65	1.343	−0.009	−0.67
N1–C6	1.344	1.345	−0.001	−0.07	1.345	−0.001	−0.07	1.354	−0.010	−0.74	1.343	0.001	0.07	1.344	0.000	0.00	1.359	−0.015	−1.12
N1–C7	1.404	1.381	0.023	1.64	1.381	0.023	1.64	1.379	0.025	1.78	1.381	0.023	1.64	1.381	0.023	1.64	1.385	0.019	1.35
N2–C3	1.327	1.307	0.020	1.51	1.307	0.020	1.51	1.319	0.008	0.60	1.305	0.022	1.66	1.305	0.022	1.66	1.324	0.003	0.23
C3–C4	1.379	1.387	−0.008	−0.58	1.387	−0.008	−0.58	1.385	−0.006	−0.44	1.387	−0.008	−0.58	1.387	−0.008	−0.58	1.397	−0.018	−1.31
C4–C5	1.343	1.376	−0.033	−2.46	1.375	−0.032	−2.38	1.380	−0.037	−2.76	1.374	−0.031	−2.31	1.374	−0.031	−2.31	1.388	−0.045	−3.35
C5–C6	1.383	1.376	0.007	0.51	1.376	0.007	0.51	1.375	0.008	0.58	1.376	0.007	0.51	1.375	0.008	0.58	1.384	−0.001	−0.07
C7–C12	1.383	1.408	−0.025	−1.81	1.408	−0.025	−1.81	1.401	−0.018	−1.30	1.405	−0.022	−1.59	1.406	−0.023	−1.66	1.407	−0.024	−1.74
C7–C13	1.404	1.412	−0.008	−0.57	1.412	−0.008	−0.57	1.404	0.000	0.00	1.409	−0.005	−0.36	1.409	−0.005	−0.36	1.410	−0.006	−0.43
C12–N14	1.141	1.142	−0.001	−0.09	1.142	−0.001	−0.09	1.149	−0.008	−0.70	1.136	0.005	0.44	1.136	0.005	0.44	1.159	−0.018	−1.58
C13–N15	1.153	1.140	0.013	1.13	1.140	0.013	1.13	1.146	0.007	0.61	1.134	0.019	1.65	1.134	0.019	1.65	1.157	−0.004	−0.35
		SD =	0.018	1.37	SD =	0.018	1.35	SD =	0.016	1.19	SD =	0.018	1.38	SD =	0.019	1.39	SD =	0.016	1.22
		D95*			MNDO			MINDO/3			ZINDO			AM1			PM3		
N1–N2	1.334	1.317	0.017	1.27	1.337	−0.003	−0.22	1.291	0.043	3.22	1.337	−0.003	−0.22	1.341	−0.007	−0.52	1.356	−0.022	−1.65
N1–C6	1.344	1.344	0.000	0.00	1.405	−0.061	−4.54	1.391	−0.047	−3.50	1.405	−0.061	−4.54	1.397	−0.053	−3.94	1.396	−0.052	−3.87
N1–C7	1.404	1.382	0.022	1.57	1.380	0.024	1.71	1.350	0.054	3.85	1.380	0.024	1.71	1.379	0.025	1.78	1.368	0.036	2.56
N2–C3	1.327	1.308	0.019	1.43	1.349	−0.022	−1.66	1.339	−0.012	−0.90	1.349	−0.022	−1.66	1.346	−0.019	−1.43	1.351	−0.024	−1.81
C3–C4	1.379	1.393	−0.014	−1.02	1.413	−0.034	−2.47	1.395	−0.016	−1.16	1.413	−0.034	−2.47	1.410	−0.031	−2.25	1.395	−0.016	−1.16
C4–C5	1.343	1.379	−0.036	−2.68	1.399	−0.056	−4.17	1.410	−0.067	−4.99	1.399	−0.056	−4.17	1.393	−0.050	−3.72	1.393	−0.050	−3.72
C5–C6	1.383	1.381	0.002	0.14	1.403	−0.020	−1.45	1.390	−0.007	−0.51	1.403	−0.020	−1.45	1.399	−0.016	−1.16	1.388	−0.005	−0.36
C7–C12	1.383	1.412	−0.029	−2.10	1.415	−0.032	−2.31	1.443	−0.060	−4.34	1.415	−0.032	−2.31	1.415	−0.032	−2.31	1.414	−0.031	−2.24
C7–C13	1.404	1.416	−0.012	−0.85	1.417	−0.013	−0.93	1.446	−0.042	−2.99	1.417	−0.013	−0.93	1.416	−0.012	−0.85	1.415	−0.011	−0.78
C12–N14	1.141	1.144	−0.003	−0.26	1.164	−0.023	−2.02	1.161	−0.020	−1.75	1.164	−0.023	−2.02	1.165	−0.024	−2.10	1.161	−0.020	−1.75
C13–N15	1.153	1.143	0.010	0.87	1.163	−0.010	−0.87	1.162	−0.009	−0.78	1.163	−0.010	−0.87	1.163	−0.010	−0.87	1.161	−0.008	−0.69
		SD =	0.019	1.42	SD =	0.024	1.74	SD =	0.038	2.81	SD =	0.024	1.74	SD =	0.022	1.58	SD =	0.024	1.74

TABLE II Experimental and calculated bond angles (°) of pyridazinium dicyanomethylide **1a**

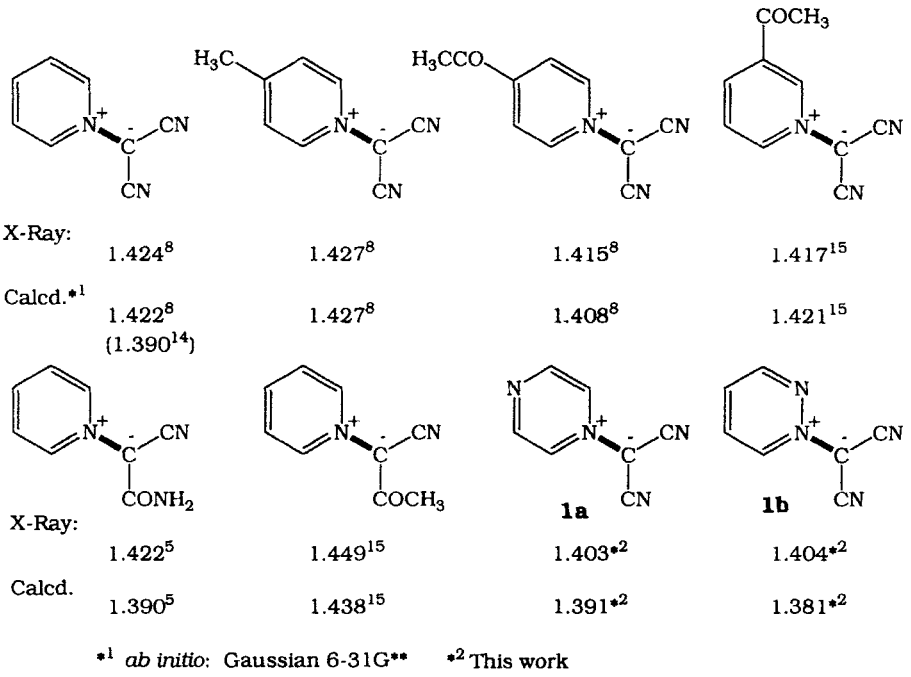
		STO-3G			STO-3G*			3-21G*			3-21G*			4-31G			6-31G		
Atom	X-ray	Cal.	Dif.	% of dif.	Cal.	Dif.	% of dif.	Cal.	Dif.	% of dif.	Cal.	Dif.	% of dif.	Cal.	Dif.	% of dif.	Cal.	Dif.	% of dif.
N1–N2–C3	115.4	114.6	0.8	0.69	114.6	0.8	0.69	117.6	−2.2	−1.91	117.6	−2.2	−1.91	119.0	−3.6	−3.12	119.0	−3.6	−3.12
N1–C7–C12	120.3	119.3	1.0	0.83	119.3	1.0	0.83	118.5	1.8	1.50	118.5	1.8	1.50	118.5	1.8	1.50	118.5	1.8	1.50
N1–C7–C13	118.2	118.5	−0.3	−0.25	118.5	−0.3	−0.25	119.7	−1.5	−1.27	119.7	−1.5	−1.27	119.4	−1.2	−1.02	119.4	−1.2	−1.02
N2–N1–C6	123.6	122.5	1.1	0.89	122.5	1.1	0.89	121.4	2.2	1.78	121.4	2.2	1.78	121.2	2.4	1.94	121.4	2.2	1.78
N2–N1–C7	115.0	115.1	−0.1	−0.09	115.1	−0.1	−0.09	115.2	−0.2	−0.17	115.2	−0.2	−0.17	116.0	−1.0	−0.87	116.0	−1.0	−0.87
N2–C3–C4	125.2	126.2	−1.0	−0.80	126.2	−1.0	−0.80	124.6	0.6	0.48	124.6	0.6	0.48	123.8	1.4	1.12	123.7	1.5	1.20
C3–C4–C5	117.3	117.2	0.1	0.09	117.2	0.1	0.09	116.6	0.7	0.60	116.6	0.7	0.60	116.4	0.9	0.77	116.4	0.9	0.77
C4–C5–C6	119.1	119.6	−0.5	−0.42	119.6	−0.5	−0.42	119.7	−0.6	−0.50	119.7	−0.6	−0.50	119.7	−0.6	−0.50	119.7	−0.6	−0.50
C5–C6–N1	119.4	120.0	−0.6	−0.50	120.0	−0.6	−0.50	120.1	−0.7	−0.59	120.1	−0.7	−0.59	120.0	−0.6	−0.50	119.9	−0.5	−0.42
C6–N1–C7	121.4	122.4	−1.0	−0.82	122.4	−1.0	−0.82	123.4	−2.0	−1.65	123.4	−2.0	−1.65	122.8	−1.4	−1.15	122.7	−1.3	−1.07
C7–C12–N14	179.8	179.9	−0.1	−0.06	179.9	−0.1	−0.06	179.6	0.2	0.11	179.6	0.2	0.11	178.0	1.8	1.00	177.9	1.9	1.06
C7–C13–N15	176.3	178.7	−2.4	−1.36	178.7	−2.4	−1.36	177.6	−1.3	−0.74	177.6	−1.3	−0.74	178.6	−2.3	−1.30	178.9	−2.6	−1.47
C12–C7–C13	121.6	122.2	−0.6	−0.49	122.2	−0.6	−0.49	121.7	−0.1	−0.08	121.7	−0.1	−0.08	122.1	−0.5	−0.41	122.1	−0.5	−0.41
		SD=	0.94	0.68	SD=	0.94	0.68	SD=	1.35	1.11	SD=	1.35	1.11	SD=	1.78	1.40	SD=	1.80	1.14
		6-31G*			6-31G**			6-311G			6-311G*			6-311G**			D95		
N1–N2–C3	115.4	118.8	−3.4	−2.95	118.8	−3.4	−2.95	118.9	−3.5	−3.03	118.9	−3.5	−3.03	118.9	−3.5	−3.03	118.9	−3.5	−3.03
N1–C7–C12	120.3	118.6	1.7	1.41	118.6	1.7	1.41	118.6	1.7	1.41	118.7	1.6	1.33	118.7	1.6	1.33	118.8	1.5	1.25
N1–C7–C13	118.2	119.6	−1.4	−1.18	119.6	−1.4	−1.18	119.3	−1.1	−0.93	119.6	−1.4	−1.18	119.6	−1.4	−1.18	119.7	−1.5	−1.27
N2–N1–C6	123.6	121.8	1.8	1.46	121.8	1.8	1.46	121.3	2.3	1.86	121.8	1.8	1.46	121.9	1.7	1.38	121.5	2.1	1.70
N2–N1–C7	115.0	115.9	−0.9	−0.78	115.9	−0.9	−0.78	115.9	−0.9	−0.78	115.9	−0.9	−0.78	116.0	−1.0	−0.87	115.8	−0.8	−0.70
N2–C3–C4	125.2	124.3	0.9	0.72	124.3	0.9	0.72	123.8	1.4	1.12	124.3	0.9	0.72	124.2	1.0	0.80	123.8	1.4	1.12
C3–C4–C5	117.3	115.8	1.5	1.28	115.8	1.5	1.28	116.4	0.9	0.77	115.8	1.5	1.28	115.8	1.5	1.28	116.3	1.0	0.85
C4–C5–C6	119.1	119.3	−0.2	−0.17	119.3	−0.2	−0.17	119.7	−0.6	−0.50	119.2	−0.1	−0.08	119.2	−0.1	−0.08	119.6	−0.5	−0.42
C5–C6–N1	119.4	120.0	−0.6	−0.50	120.0	−0.6	−0.50	120.0	−0.6	−0.50	120.0	−0.6	−0.50	120.0	−0.6	−0.50	120.0	−0.6	−0.50
C6–N1–C7	121.4	122.3	−0.9	−0.74	122.3	−0.9	−0.74	122.8	−1.4	−1.15	122.2	−0.8	−0.66	122.2	−0.8	−0.66	122.8	−1.4	−1.15
C7–C12–N14	179.8	177.3	2.5	1.39	177.2	2.6	1.45	178.3	1.5	0.83	177.6	2.2	1.22	177.5	2.3	1.28	179.1	0.7	0.39
C7–C13–N15	176.3	177.9	−1.6	−0.91	177.9	−1.6	−0.91	178.8	−2.5	−1.42	178.0	−1.7	−0.96	178.0	−1.7	−0.96	178.5	−2.2	−1.25
C12–C7–C13	121.6	121.8	−0.2	−0.16	121.8	−0.2	−0.16	122.1	−0.5	−0.41	121.7	−0.1	−0.08	121.8	−0.2	−0.16	121.5	0.1	0.08
		SD=	1.40	1.03	SD=	1.68	1.31	SD=	1.73	1.36	SD=	1.65	1.30	SD=	1.66	1.30	SD=	1.62	1.31
		D95*			MNDO			MINDO/3			ZINDO			AM1			PM3		
N1–N2–C3	115.4	118.7	−3.3	−2.86	119.3	−3.9	−3.38	122.5	−7.1	−6.15	119.3	−3.9	−3.38	118.7	−3.3	−2.86	120.5	−5.1	−4.42
N1–C7–C12	120.3	118.8	1.5	1.25	121.1	−0.8	−0.67	122.3	−2.0	−1.66	121.1	−0.8	−0.67	121.6	−1.3	−1.08	121.7	−1.4	−1.16
N1–C7–C13	118.2	119.8	−1.6	−1.35	120.4	−2.2	−1.86	118.9	−0.7	−0.59	120.4	−2.2	−1.86	121.0	−2.8	−2.37	121.4	−3.2	−2.71
N2–N1–C6	123.6	122.0	1.6	1.29	121.6	2.0	1.62	119.7	3.9	3.16	121.5	2.1	1.70	120.8	2.8	2.27	119.6	4.0	3.24
N2–N1–C7	115.0	115.8	−0.8	−0.70	115.3	−0.3	−0.26	114.8	0.2	0.17	115.3	−0.3	−0.26	119.1	−4.1	−3.57	118.5	−3.5	−3.04
N2–C3–C4	125.2	124.3	0.9	0.72	123.4	1.8	1.44	123.1	2.1	1.68	123.4	1.8	1.44	124.3	0.9	0.72	122.1	3.1	2.48
C3–C4–C5	117.3	115.8	1.5	1.28	117.0	0.3	0.26	114.6	2.7	2.30	117.0	0.3	0.26	116.5	0.8	0.68	117.9	−0.6	−0.51
C4–C5–C6	119.1	119.2	−0.1	−0.08	119.6	−0.5	−0.42	120.6	−1.5	−1.26	119.6	−0.5	−0.42	119.2	−0.1	−0.08	119.7	−0.6	−0.50
C5–C6–N1	119.4	120.1	−0.7	−0.59	119.3	0.1	0.08	119.6	−0.2	−0.17	119.3	0.1	0.08	120.4	−1.0	−0.84	120.2	−0.8	−0.67
C6–N1–C7	121.4	122.2	−0.8	−0.66	123.1	−1.7	−1.40	125.5	−4.1	−3.38	123.1	−1.7	−1.40	120.0	1.4	1.15	121.9	−0.5	−0.41
C7–C12–N14	179.8	177.5	2.3	1.28	178.5	1.3	0.72	178.2	1.6	0.89	178.5	1.3	0.72	179.2	0.6	0.33	179.0	0.8	0.44
C7–C13–N15	176.3	178.1	−1.8	−1.02	177.5	−1.2	−0.68	176.0	0.3	0.17	177.5	−1.2	−0.68	177.6	−1.3	−0.74	177.4	−1.1	−0.62
C12–C7–C13	121.6	121.5	0.1	0.08	118.5	3.1	2.55	118.8	2.8	2.30	118.5	3.1	2.55	117.4	4.2	3.45	116.9	4.7	3.87
		SD=	1.62	1.27	SD=	1.91	1.57	SD=	3.04	2.54	SD=	1.92	1.57	SD=	2.39	1.99	SD=	2.89	2.41

TABLE III Experimental and calculated bond lengths (Å) of pyradinium dicyanomethylide **1b**

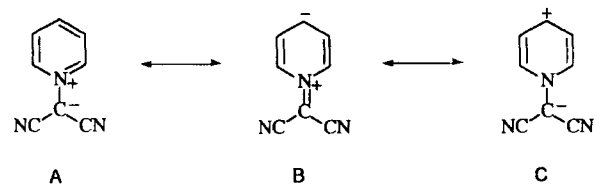
		STO-3G			STO-3G*			3-21G			3-21G*			4-31G*			6-31G		
Atom	X-ray	Cal.	Dif.	% of dif.	Cal.	Dif.	% of dif.	Cal.	Dif.	% of dif.	Cal.	Dif.	% of dif.	Cal.	Dif.	% of dif.	Cal.	Dif.	% of dif.
N1–C2	1.366	1.386	−0.020	−1.46	1.386	−0.020	−1.46	1.361	0.005	0.37	1.361	0.005	0.37	1.357	0.009	0.66	1.360	0.006	0.44
N1–C6	1.366	1.386	−0.020	−1.46	1.386	−0.020	−1.46	1.361	0.005	0.37	1.361	0.005	0.37	1.357	0.009	0.66	1.360	0.006	0.44
N1–C7	1.403	1.340	0.063	4.49	1.400	0.003	0.21	1.397	0.006	0.43	1.397	0.006	0.43	1.395	0.008	0.57	1.398	0.005	0.36
C2–C3	1.371	1.376	−0.005	−0.36	1.376	−0.005	−0.36	1.370	0.001	0.07	1.370	0.001	0.07	1.371	0.000	0.00	1.375	−0.004	−0.29
C3–N4	1.339	1.358	−0.019	−1.42	1.358	−0.019	−1.42	1.330	0.009	0.67	1.330	0.009	0.67	1.327	0.012	0.90	1.331	0.008	0.60
N4–C5	1.339	1.358	−0.019	−1.42	1.358	−0.019	−1.42	1.330	0.009	0.67	1.330	0.009	0.67	1.327	0.012	0.90	1.331	0.008	0.60
C5–C6	1.371	1.376	−0.005	−0.36	1.376	−0.005	−0.36	1.370	0.001	0.07	1.370	0.001	0.07	1.371	0.000	0.00	1.375	−0.004	−0.29
C7–C12	1.404	1.423	−0.019	−1.35	1.423	−0.019	−1.35	1.393	0.011	0.78	1.393	0.011	0.78	1.394	0.010	0.71	1.399	0.005	0.36
C7–C13	1.404	1.423	−0.019	−1.35	1.423	−0.019	−1.35	1.393	0.011	0.78	1.393	0.011	0.78	1.394	0.010	0.71	1.399	0.005	0.36
C12–N14	1.147	1.161	−0.014	−1.22	1.161	−0.014	−1.22	1.146	0.001	0.09	1.146	0.001	0.09	1.149	−0.002	−0.17	1.154	−0.007	−0.61
C13–N15	1.147	1.161	−0.014	−1.22	1.161	−0.014	−1.22	1.146	0.001	0.09	1.146	0.001	0.09	1.149	−0.002	−0.17	1.154	−0.007	−0.61
		SD =	0.024	1.75	SD =	0.008	0.58	SD =	0.004	0.29	SD =	0.004	0.29	SD =	0.006	0.43	SD =	0.006	0.47
		6-31G*			6-31G**			6-311G			6-311G*			6-311G**			D95		
N1–C2	1.366	1.350	0.016	1.17	1.350	0.016	1.17	1.359	0.007	0.51	1.348	0.018	1.32	1.348	0.018	1.32	1.364	0.002	0.15
N1–C6	1.366	1.350	0.016	1.17	1.350	0.016	1.17	1.359	0.007	0.51	1.348	0.018	1.32	1.348	0.018	1.32	1.364	0.002	0.15
N1–C7	1.403	1.391	0.012	0.86	1.391	0.012	0.86	1.397	0.006	0.43	1.391	0.012	0.86	1.390	0.013	0.93	1.402	0.001	0.07
C2–C3	1.371	1.375	−0.004	−0.29	1.375	−0.004	−0.29	1.373	−0.002	−0.15	1.374	−0.003	−0.22	1.374	−0.003	−0.22	1.383	−0.012	−0.88
C3–N4	1.339	1.318	0.021	1.57	1.318	0.021	1.57	1.331	0.008	0.60	1.317	0.022	1.64	1.317	0.022	1.64	1.336	0.003	0.22
N4–C5	1.339	1.318	0.021	1.57	1.318	0.021	1.57	1.331	0.008	0.60	1.317	0.022	1.64	1.317	0.022	1.64	1.336	0.003	0.22
C5–C6	1.371	1.375	−0.004	−0.29	1.375	−0.004	−0.29	1.373	−0.002	−0.15	1.374	−0.003	−0.22	1.374	−0.003	−0.22	1.383	−0.012	−0.88
C7–C12	1.404	1.407	−0.003	−0.21	1.407	−0.003	−0.21	1.399	0.005	0.36	1.405	−0.001	−0.07	1.405	−0.001	−0.07	1.405	−0.001	−0.07
C7–C13	1.404	1.407	−0.003	−0.21	1.407	−0.003	−0.21	1.399	0.005	0.36	1.405	−0.001	−0.07	1.405	−0.001	−0.07	1.405	−0.001	−0.07
C12–N14	1.147	1.142	0.005	0.44	1.142	0.005	0.44	1.149	−0.002	−0.17	1.136	0.011	0.96	1.136	0.011	0.96	1.159	−0.012	−1.05
C13–N15	1.147	1.142	0.005	0.44	1.142	0.005	0.44	1.149	−0.002	−0.17	1.136	0.011	0.96	1.136	0.011	0.96	1.159	−0.012	−1.05
		SD =	0.010	0.74	SD =	0.010	0.74	SD =	0.004	0.33	SD =	0.010	0.75	SD =	0.010	0.75	SD =	0.007	0.54
		D95*			6-31 + G			MNDO			MINDO/3			AM1			PM3		
N1–C2	1.366	1.351	0.015	1.10	1.360	0.006	0.44	1.401	−0.035	−2.56	1.389	−0.023	−1.68	1.388	−0.022	−1.61	1.394	−0.028	−2.05
N1–C6	1.366	1.351	0.015	1.10	1.360	0.006	0.44	1.399	−0.033	−2.42	1.384	−0.018	−1.32	1.383	−0.017	−1.24	1.389	−0.023	−1.68
N1–C7	1.403	1.391	0.012	0.86	1.398	0.005	0.36	1.383	0.020	1.43	1.357	0.046	3.28	1.373	0.030	2.14	1.374	0.029	2.07
C2–C3	1.371	1.379	−0.008	−0.58	1.376	−0.005	−0.36	1.405	−0.034	−2.48	1.397	−0.026	−1.90	1.349	0.022	1.60	1.391	−0.020	−1.46
C3–N4	1.339	1.320	0.019	1.42	1.331	0.008	0.60	1.352	−0.013	−0.97	1.338	0.001	0.07	1.349	−0.010	−0.75	1.356	−0.017	−1.27
N4–C5	1.339	1.320	0.019	1.42	1.331	0.008	0.60	1.351	−0.012	−0.90	1.337	0.002	0.15	1.348	−0.009	−0.67	1.354	−0.015	−1.12
C5–C6	1.371	1.379	−0.008	−0.58	1.376	−0.005	−0.36	1.406	−0.035	−2.55	1.393	−0.022	−1.60	1.409	−0.038	−2.77	1.394	−0.023	−1.68
C7–C12	1.404	1.412	−0.008	−0.57	1.399	0.005	0.36	1.414	−0.010	−0.71	1.445	−0.041	−2.92	1.413	−0.009	−0.64	1.411	−0.007	−0.50
C7–C13	1.404	1.412	−0.008	−0.57	1.399	0.005	0.36	1.415	−0.011	−0.78	1.447	−0.043	−3.06	1.416	−0.012	−0.85	1.413	−0.009	−0.64
C12–N14	1.147	1.144	0.003	0.26	1.153	−0.006	−0.52	1.165	−0.018	−1.57	1.163	−0.016	−1.39	1.165	−0.018	−1.57	1.162	−0.015	−1.31
C13–N15	1.147	1.144	0.003	0.26	1.153	−0.006	−0.52	1.164	−0.017	−1.48	1.163	−0.016	−1.39	1.165	−0.018	−1.57	1.162	−0.015	−1.31
		SD =	0.012	0.84	SD =	0.006	0.46	SD =	0.016	1.19	SD =	0.024	1.75	SD =	0.019	1.43	SD =	0.015	1.11

TABLE IV Experimental and calculated bond angles (°) of pyradinium dicyanomethylide **1b**

		STO-3G			STO-3G*			3-21G			3-21G*			4-31G			6-31G		
Atom	X-ray	Cal.	Dif.	% of dif.	Cal.	Dif.	% of dif.	Cal.	Dif.	% of dif.	Cal.	Dif.	% of dif.	Cal.	Dif.	% of dif.	Cal.	Dif.	% of dif.
N1-C2-C3	119.6	120.3	−0.7	−0.59	120.3	−0.7	−0.59	120.0	−0.4	−0.33	120.0	−0.4	−0.33	120.1	−0.5	−0.42	120.1	−0.5	−0.42
N1-C7-C12	118.8	118.9	−0.1	−0.08	118.9	−0.1	−0.08	118.7	0.1	0.08	118.7	0.1	0.08	118.8	0.0	0.00	118.8	0.0	0.00
N1-C7-C13	118.8	118.9	−0.1	−0.08	118.9	−0.1	−0.08	118.7	0.1	0.08	118.7	0.1	0.08	118.8	0.0	0.00	118.8	0.0	0.00
C2-N1-C6	117.4	116.0	1.4	1.19	116.0	1.4	1.19	117.5	−0.1	−0.09	117.5	−0.1	−0.09	117.5	−0.1	−0.09	117.5	−0.1	−0.09
C2-N1-C7	121.3	122.0	−0.7	−0.58	122.0	−0.7	−0.58	121.3	0.0	0.00	121.3	0.0	0.00	121.3	0.0	0.00	121.3	0.0	0.00
C2-C3-N4	124.6	125.1	−0.5	−0.40	125.1	−0.5	−0.40	122.8	1.8	1.44	122.8	1.8	1.44	122.7	1.9	1.52	122.8	1.8	1.44
C3-N4-C5	114.3	113.3	1.0	0.87	113.3	1.0	0.87	116.9	−2.6	−2.27	116.9	−2.6	−2.27	116.9	−2.6	−2.27	116.8	−2.5	−2.19
N4-C5-C6	124.6	125.1	−0.5	−0.40	125.1	−0.5	−0.40	122.8	1.8	1.44	122.8	1.8	1.44	122.7	1.9	1.52	122.8	1.8	1.44
C5-C6-N1	119.6	120.3	−0.7	−0.59	120.3	−0.7	−0.59	120.0	−0.4	−0.33	120.0	−0.4	−0.33	120.1	−0.5	−0.42	120.1	−0.5	−0.42
C6-N1-C7	121.3	122.0	−0.7	−0.58	122.0	−0.7	−0.58	121.3	0.0	0.00	121.3	0.0	0.00	121.3	0.0	0.00	121.3	0.0	0.00
C7-C12-N14	177.8	180.0	−2.2	−1.24	180.0	−2.2	−1.24	179.8	−2.0	−1.12	179.8	−2.0	−1.12	178.3	−0.5	−0.28	178.1	−0.3	−0.17
C7-C13-N15	177.8	180.0	−2.2	−1.24	180.0	−2.2	−1.24	179.8	−2.0	−1.12	179.8	−2.0	−1.12	178.3	−0.5	−0.28	178.1	−0.3	−0.17
C12-C7-C13	122.4	122.2	0.2	0.16	122.2	0.2	0.16	122.6	−0.2	−0.16	122.6	−0.2	−0.16	122.5	−0.1	−0.08	122.5	−0.1	−0.08
		SD=	1.02	0.71	SD=	1.02	0.71	SD=	1.31	0.99	SD=	1.31	0.99	SD=	1.12	0.93	SD=	1.06	0.91
		6-31G*			6-31G**			6-311G			6-311G*			6-311G**			D95		
N1-C2-C3	119.6	120.0	−0.4	−0.33	119.9	−0.3	−0.25	120.1	−0.5	−0.42	120.0	−0.4	−0.33	120.0	−0.4	−0.33	120.1	−0.5	−0.42
N1-C7-C12	118.8	119.0	−0.2	−0.17	119.0	−0.2	−0.17	118.8	0.0	0.00	119.0	−0.2	−0.17	119.0	−0.2	−0.17	119.1	−0.3	−0.25
N1-C7-C13	118.8	119.0	−0.2	−0.17	119.0	−0.2	−0.17	118.8	0.0	0.00	119.0	−0.2	−0.17	119.0	−0.2	−0.17	119.1	−0.3	−0.25
C2-N1-C6	117.4	117.0	0.4	0.34	117.1	0.3	0.26	117.4	0.0	0.00	117.1	0.3	0.26	117.0	0.4	0.34	117.4	0.0	0.00
C2-N1-C7	121.3	121.5	−0.2	−0.16	121.5	−0.2	−0.16	121.3	0.0	0.00	121.5	−0.2	−0.16	121.5	−0.2	−0.16	121.3	0.0	0.00
C2-C3-N4	124.6	123.8	0.8	0.64	123.8	0.8	0.64	122.9	1.7	1.36	123.8	0.8	0.64	123.8	0.8	0.64	122.9	1.7	1.36
C3-N4-C5	114.3	115.5	−1.2	−1.05	115.5	−1.2	−1.05	116.6	−2.3	−2.01	115.5	−1.2	−1.05	115.5	−1.2	−1.05	116.6	−2.3	−2.01
N4-C5-C6	124.6	123.8	0.8	0.64	123.8	0.8	0.64	122.9	1.7	1.36	123.8	0.8	0.64	123.8	0.8	0.64	122.9	1.7	1.36
C5-C6-N1	119.6	120.0	−0.4	−0.33	119.9	−0.3	−0.25	120.1	−0.5	−0.42	120.0	−0.4	−0.33	120.0	−0.4	−0.33	120.1	−0.5	−0.42
C6-N1-C7	121.3	121.5	−0.2	−0.16	121.5	−0.2	−0.16	121.3	0.0	0.00	121.5	−0.2	−0.16	121.5	−0.2	−0.16	121.3	0.0	0.00
C7-C12-N14	177.8	177.7	0.1	0.06	177.7	0.1	0.06	178.5	−0.7	−0.39	178.0	−0.2	−0.11	178.0	−0.2	−0.11	179.3	−1.5	−0.84
C7-C13-N15	177.8	177.7	0.1	0.06	177.7	0.1	0.06	178.5	−0.7	−0.39	178.0	−0.2	−0.11	178.0	−0.2	−0.11	179.3	−1.5	−0.84
C12-C7-C13	122.4	122.1	0.3	0.25	122.1	0.3	0.25	122.4	0.0	0.00	122.0	0.4	0.33	122.0	0.4	0.33	121.7	0.7	0.57
		SD=	0.54	0.46	SD=	0.52	0.45	SD=	1.02	0.84	SD=	0.54	0.46	SD=	0.54	0.45	SD=	1.16	0.90
		D95*			6-31+G			MNDO			MINDO/3			AM1			PM3		
N1-C2-C3	119.6	120.0	−0.4	−0.33	120.1	−0.5	−0.42	120.0	−0.4	−0.33	119.7	−0.1	−0.08	119.7	−0.1	−0.08	120.3	−0.7	−0.59
N1-C7-C12	118.8	119.1	−0.3	−0.25	118.8	0.0	0.00	121.5	−2.7	−2.27	122.6	−3.8	−3.20	121.1	−2.3	−1.94	121.6	−2.8	−2.36
N1-C7-C13	118.8	119.1	−0.3	−0.25	118.8	0.0	0.00	120.4	−1.6	−1.35	121.2	−2.4	−2.02	120.6	−1.8	−1.52	120.8	−2.0	−1.68
C2-N1-C6	117.4	117.1	0.3	0.26	117.5	−0.1	−0.09	116.6	0.8	0.68	115.8	1.6	1.36	117.3	0.1	0.09	117.2	0.2	0.17
C2-N1-C7	121.3	121.5	−0.2	−0.16	121.3	0.0	0.00	121.1	0.2	0.16	120.6	0.7	0.58	120.4	0.9	0.74	120.5	0.8	0.66
C2-C3-N4	124.6	123.8	0.8	0.64	122.8	1.8	1.44	123.4	1.2	0.96	124.6	0.0	0.00	123.7	0.9	0.72	121.9	2.7	2.17
C3-N4-C5	114.3	115.4	−1.1	−0.96	116.7	−2.4	−2.10	116.3	−2.0	−1.75	115.4	−1.1	−0.96	115.8	−1.5	−1.31	118.3	−4.0	−3.50
N4-C5-C6	124.6	123.8	0.8	0.64	122.8	1.8	1.44	123.4	1.2	0.96	124.6	0.0	0.00	123.7	0.9	0.72	121.9	2.7	2.17
C5-C6-N1	119.6	120.0	−0.4	−0.33	120.1	−0.5	−0.42	120.0	−0.4	−0.33	119.7	−0.1	−0.08	119.7	−0.1	−0.08	120.3	−0.7	−0.59
C6-N1-C7	121.3	121.5	−0.2	0.16	121.3	0.0	0.00	122.3	−1.0	−0.82	123.6	−2.3	−1.90	122.3	−1.0	−0.82	122.3	−1.0	−0.82
C7-C12-N14	177.8	177.9	−0.1	−0.06	178.0	−0.2	−0.11	177.3	0.5	0.28	176.4	1.4	0.79	178.6	−0.8	−0.45	177.9	−0.1	−0.06
C7-C13-N15	177.8	177.9	−0.1	−0.06	178.0	−0.2	−0.11	177.8	0.0	0.00	177.5	0.3	0.17	178.7	−0.9	−0.51	179.1	−1.3	−0.73
C12-C7-C13	122.4	121.7	0.7	0.57	122.4	0.0	0.00	118.1	4.3	3.51	116.2	6.2	5.07	118.3	4.1	3.35	117.6	4.8	3.92
		SD=	0.55	0.46	SD=	1.03	0.90	SD=	1.77	1.46	SD=	2.42	1.99	SD=	1.64	0.90	SD=	2.41	1.99



SCHEME 1 Experimental (X-ray) and calculated C–N bond lengths (Å) of representative dicyanomethylides.



SCHEME 2 Resonance structures of pyridinimum dicyanomethylide.

lengths, while the STO-3G and STO-3G* methods gave the smallest standard deviation (0.68%) from X-ray data with respect to the bond angles. Thus, in average, the 6-311G method seems to be best for reproduction of the *total* geometry (1.15%) of **1a**. As mentioned above, reproduction of the total geometry was not greatly improved by higher levels of *ab initio* calculations; even semi-empirical calculations like the AM1 method afforded a standard deviation of 1.58% (*vs.* 1.20 by 4-31G). In contrast with **1a**, pyrazinium dicyanomethylide **1b** seems to need higher levels of *ab initio* calculations to reproduce the bond angles. Indeed, the smallest standard deviations (0.45, 0.46%) for bond angles were obtained by 6-31G*, 6-311G* and D-95 respectively, while the deviation (0.29) for bond lengths was obtained by 3-21G and 3-21G*. Thus, the 6-31G* level or higher levels of calculations (0.58, 0.60% on average) are presumably appropriate for reasonable representation of the geometry of **1b**.

In conclusion, the *ab initio* methods provide good agreement with experiments for the total geometry of **1b**, whereas this was not so much the case for **1a**, especially for reproduction of bond lengths.

Further work on comparative studies of related ylides, in particular non-planar ones, between X-ray data and molecular orbital

TABLE V Standard deviations (%) of the calculated bond lengths and angles from the experimental (X-ray) values

	1a			1b		
	Length	Angle	Ave.	Length	Angle	Ave.
STO-3G	1.71	[0.68]	1.19	1.75	0.71	1.23
STO-3G*	1.71	[0.68]	1.19	0.58	0.71	0.65
3-21G	1.40	1.11	1.25	[0.29]	0.99	0.64
3-21G*	1.40	1.11	1.25	[0.29]	0.99	0.64
4-31G	[1.20]	1.40	1.30	0.43	0.93	0.68
6-31G	1.21	1.14	1.17	0.47	0.92	0.69
6-31G*	1.37	1.03	1.20	0.75	0.46	0.60
6-31G**	1.35	1.03	1.19	0.75	[0.45]	0.60
6-311G	[1.20]	1.11	[1.15]	0.33	0.84	[0.58]
6-311G*	1.38	1.00	1.19	0.75	0.46	0.60
6-311G**	1.39	1.31	1.35	0.45	0.75	0.60
D-95	1.22	1.31	1.27	0.54	0.90	0.72
D-95*	1.42	1.27	1.34	0.84	0.46	0.65
MINDO/3	2.08	2.55	2.31	1.75	1.99	1.87
MNDO	1.74	1.57	1.66	1.19	1.46	1.33
AM1	1.58	1.56	1.58	1.43	0.90	1.16
PM3	1.74	2.00	1.87	1.11	1.99	1.55

calculations specifically including the Density Functional Theory Approach (DFT) Method, as well as on transition state calculations of 1,3-dipolar cycloadditions of cycloimmonium ylides based upon the established structures by X-ray analyses, is in progress and will be the subject of further communications.

EXPERIMENTAL SECTION

Pyridazinium ylide **1a** and pyrazinium ylide **1b** were prepared from tetracyanoethylene oxide and pyridazine and pyrazine, respectively, based upon the method by Linn *et al.* [10]. Their physical and spectroscopic data have already been reported by us [16].

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[11] Data were collected at $T = 22°C$ on a Rigaku AFC5S diffractometer; **1a**: $C_7H_4N_4$, $M = 144.14$, yellow prism, dimensions $0.200 \times 0.480 \times 1.000$ mm, orthorhombic, space group = Pnma (No. 62), $a = 9.069(4)$ Å, $b = 6.411(4)$ Å $c = 12.299(3)$ Å, $U = 715.1(5)$ Å^3, $Z = 4$, $Dc = 1.3339$ gcm^{-3} $F(000) = 296$. Mo-Kα radiation

($\lambda = 0.71069$ Å) $\mu = 0.084\,mm^{-1}$, ω-2Θ scan mode with ω scan width $= 1.73 + 0.30\tan\theta$, ω scan speed $32.0\,deg\,min^{-1}$, 989 reflections were collected in the range $37.72 < 2\Theta < 39.87$. The structure was solved by direct methods [17] using full-matrix least squares on F for all non-hydrogen atoms using Lorenz polarization and absorption corrections to give $R = 0.052$, and $R_w = 0.066$ for 581 independent observed reflections with $I > 2.00\sigma(I)$ and 80 variables for $2\theta_{max} = 55.0°$. The final difference map maximum and minimum were 0.25 and -0.21 e Å^{-3}, respectively. **1b**: $C_7H_4N_4$, $M =$ 144.14, yellow plate, dimensions $0.060 \times 0.320 \times$ 880 mm, monoclinic, space group $= P2_1/m$ (No. 11), $a = 3.824(5)$ Å, $b = 12.593(3)$ Å, $c = 6.685(3)$ Å, $\beta = 91.80(6)°$, $U = 321.8\,(4)$ Å^3, $Z = 2$, $Dc = 1.487\,gcm^{-3}$, $F(000) = 148$. Mo-Kα radiation ($\lambda = 0.71069$ Å) $\mu = 0.094\,mm^{-1}$, ω-2Θ scan mode with ω scan width $= 1.68 + 0.30\tan\theta$, ω scan speed $16.0\,deg\,min^{-1}$, 876 reflections were collected in the range $38.56 < 2\theta < 39.90$ and 769 unique reflections ($R_{int} = 0.011$ 1) 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 $R = 0.052$, and $R_w = 0.063$ for 599 independent observed reflections with $I > 2.00\sigma(I)$ and 56 variables for $2\theta_{max} = 55.0°$. The final difference map maximum and minimum were 0.28 and $-0.26\,e$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 [18–20]. All calculations were performed using the TEXAN [21] crystallographic software package from Molecular Structure Corporation.

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