**Molecular structure, linear and nonlinear optical properties of piperazine-1,4-diium bis 2,4,6-trinitrophenolate: A theoretical investigation**

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**Table S1.** The coordinates of the optimized structure of the piperazine–1,4–diium bis 2,4,6–trinitrophenolate obtained at B3LYP/6–311++G(d,p) level.

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Atom Type Coordinates (Angstroms)

X Y Z

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C 1.07298200 -1.08856900 0.00513100

C 2.45239000 -1.34110200 -0.06578000

H 2.78765100 -2.36360000 -0.14351600

C 3.35403500 -0.28811400 -0.03323100

C 2.93858000 1.02861500 0.05373300

H 3.64711300 1.84298700 0.07187500

C 1.56932600 1.29006800 0.09503400

C 0.57737600 0.25885300 0.10288800

N 0.21506300 -2.22329100 -0.04498400

N 1.19489100 2.70206900 0.13600500

N 4.79556200 -0.57588200 -0.10277700

O -1.03541000 -2.06897100 0.11523100

O 0.71426700 -3.35047600 -0.23838200

O 0.11428000 3.06682600 -0.32741400

O 2.01797900 3.47574100 0.63264500

O 5.57101300 0.37391100 -0.11538500

O 5.14271300 -1.75015800 -0.15007500

O -0.66151400 0.63087300 0.21460000

C -3.52306600 1.05477400 -0.53066500

H -2.94551700 1.51461000 -1.33536300

H -3.40147700 1.70714800 0.33933600

C -3.68423500 -0.97521800 0.83243100

H -3.57885700 -0.43211300 1.77664800

H -3.21144600 -1.94597500 0.97499000

N -2.91845200 -0.24755600 -0.19328600

H -1.57999100 0.07471100 0.12917400

H -2.81580200 -0.83439800 -1.02210100

C -5.14964500 -1.14327900 0.46517100

H -5.73554700 -1.56188900 1.28735600

H -5.28482100 -1.77056100 -0.41878000

C -4.98805000 0.96054900 -0.93298400

H -5.12317600 0.40893000 -1.86590000

H -5.45890700 1.94253300 -1.03281700

N -5.76730600 0.20300100 0.12530700

H -6.74158200 0.07172900 -0.18648700

H -5.82073500 0.77606800 0.98359100

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**Table S2**

The calculated wavenumbers (cm–1) and assignments for piperazine–1,4–diium bis 2,4,6–trinitrophenolate using the B3LYP/6–311+G(d,p) level. When available, comparisons with experiment are made.

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| **N** | | **Exp IR a** | **IR Scaled** | **IInfrared** | **Characterization of normal modes with PED (%)** |
| 102 | | 3318 | 3322 | 1.9851 | νasNHPi (100) |
| 101 | | 3207 b | 3273 | 15.5802 | νsNHPi (100) |
| 100 | | 3100 c | 3109 | 13.1345 | νCHPh (99) |
| 99 | |  | 3097 | 27.6352 | νCHPh (99) |
| 98 | |  | 3072 | 10.7448 | νasCH2Pi (93) |
| 97 | | 3068 | 3070 | 2.6869 | νasCH2Pi (94) |
| 96 | |  | 3052 | 486.1855 | νOH (98) |
| 95 | |  | 3035 | 9.5044 | νasCH2Pi (84) |
| 94 | |  | 3034 | 31.0236 | νasCH2Pi (83) |
| 93 | |  | 2922 | 3.6476 | νsCH2Pi (91) |
| 92 | |  | 2921 | 12.7853 | νsCH2Pi (92) |
| 91 | |  | 2865 | 64.9261 | νsCH2Pi (99) |
| 90 | | 2841 | 2861 | 15.6592 | νsCH2Pi (99) |
| 89 | |  | 2330 | 4143.2712 | νsNHPi (88) |
| 88 | |  | 1736 | 55.6123 | δHNHPi (66); δNHPi…N (13) |
| 87 | | 1624 | 1632 | 98.9280 | νasNO2 (18); νCCPh (43); δHOC (16) |
| 86 | |  | 1618 | 248.6823 | νasNO2 (18); νCCPh (34). |
| 85 | | 1436 | 1467 | 133.9438 | νasNO2 (61); δHOC (22) |
| 84 | |  | 1461 | 168.4095 | νasNO2 (59); νCCPh (23) |
| 83 | |  | 1459 | 18.7990 | δCNHPi (50); τ HNHPi…N (11); τONPh…HN (14); τCNHPi…N (12) |
| 82 | |  | 1458 | 76.7494 | νCCPh (16); δHOC (12); δHCHPi(18); τHCCNPi (12) |
| 81 | |  | 1456 | 8.5589 | νCC Ph (10); δHCHPi (17); δHCHPi (29); τHCCNPi (11) |
| 80 | |  | 1454 | 4.2305 | δHNCPh (37); δHCHPi (29) |
| 79 | |  | 1438 | 15.8046 | δHNCPh (21); δHCHPi (23); δHCHPi (20); τHCNCPi (11) |
| 78 | |  | 1434 | 13.5926 | δHCHPi (51); δHCHPi (34); τHCNCPi (10) |
| 77 | |  | 1428 | 0.0756 | δHCHPi (26); δHCHPi (53); τHCNCPi (11) |
| 76 | |  | 1426 | 153.5992 | νOC (18); δHOC (14); δHCCPh (20); δCCCPh (12) |
| 75 | |  | 1391 | 14.6342 | τHNHPi…N (50) |
| 74 | |  | 1370 | 25.7963 | νCCPh (17); νCCPh (15); νNCPh (14); δHCCPh (13) |
| 73 | |  | 1366 | 15.1860 | wHCNCPi (10); wHCCNPi (33) |
| 72 | |  | 1354 | 8.7753 | wHCNCPi (50) |
| 71 | |  | 1352 | 128.8998 | νCCPh (29); νNCPh (16); νsNO2 (12) |
| 70 | |  | 1345 | 1.3426 | wHCNCPi (54) |
| 69 | |  | 1343 | 181.7078 | νsNO2 (56) |
| 68 | |  | 1335 | 0.8024 | δHCCPi (11); δHCNPi (22); τHCNCPi (12); τCNHPi…N (10) |
| 67 | |  | 1324 | 0.0392 | δHCCPi (17); wHCCNPi (49) |
| 66 | | 1321 | 1322 | 571.4059 | νsNO2 (73) |
| 65 | |  | 1314 | 4.5167 | δHCNPi (23); δHCCPi (21); τCNHPi…N (15) |
| 64 | |  | 1301 | 110.1068 | νCCPh (13); νNCPh (11); νsNO2 (11); δHCCPh (15) |
| 63 | 1273 | | 1279 | 88.1991 | νCCPh (22); νOC (43); δHCCPh (10) |
| 62 |  | | 1235 | 1.5854 | δHCCPi (36); δHCNPi (20) |
| 61 |  | | 1206 | 172.2854 | νsNO2 (54) |
| 60 |  | | 1166 | 32.5627 | δHCCPh (50) |
| 59 |  | | 1165 | 101.3979 | νsNO2 (18); ρ CNHPi (10); τCNCCPi (13) |
| 58 |  | | 1155 | 4.0559 | νNCPi (18); δHCNPi (19); δHCCPi (22); τHNHPi…N (10) |
| 57 |  | | 1123 | 32.0801 | νNCPi (66) |
| 56 |  | | 1122 | 258.5659 | νCCPh (21); νsNO2 (18); νNCPh (15); δCCCPh (16) |
| 55 |  | | 1063 | 77.5732 | νCCPh (14); δHCCPh (48) |
| 54 |  | | 1048 | 9.4011 | νNCPi (63) |
| 53 |  | | 1029 | 2.7207 | νNCPi (18); ρ CNHPi (20); τHCCNPi (10) |
| 52 |  | | 997 | 12.4630 | νCCPi (28); νNCPi (17); τHCCNPi (10) |
| 51 |  | | 988 | 14.8236 | τHCNCPi (25); τHCCNPi (15); τCNCCPi (13) |
| 50 |  | | 932 | 52.4083 | νCCPi (21); ρ HNHPi (13); δCNHPi (12); τCCNHPi (14) |
| 49 |  | | 922 | 41.6500 | νsNO2 (12); νNCPh (31); δONO (19) |
| 48 |  | | 913 | 30.3561 | νNCPh (15); νsNO2 (18); νNCPh (13); δONO (18) |
| 47 |  | | 911 | 32.7839 | wHCCNPh (69) |
| 46 |  | | 906 | 4.0777 | νNCPi (22); νNCPi (11); wHCCNPh (40) |
| 45 |  | | 905 | 7.1332 | νNCPi (21); νNCPi (11); τHCCNPh (41) |
| 44 |  | | 880 | 0.5552 | δCNCPi (13); δCCNPi (22); τHCCNPi (11) |
| 43 |  | | 842 | 65.9695 | τHOCCPh (84) |
| 42 |  | | 836 | 22.7109 | νOC (11); δONO (11); δCCCPh (31) |
| 41 |  | | 828 | 0.0566 | νNCPi (16); τHCNCPi (35); τHCCNPi (27) |
| 40 |  | | 819 | 1.3594 | νCCPi (17); νNCPi (42) |
| 39 |  | | 806 | 51.6325 | νsNO2 (12); δONO (36) |
| 38 |  | | 780 | 20.0663 | *β*OCONPh (48) |
| 37 |  | | 743 | 172.8935 | *ν*NCPi (16); δHNCPh (13); τHNCCpi (47) |
| 36 |  | | 736 | 15.9253 | βOCONPh (50) |
| 35 |  | | 724 | 48.9737 | *δ*ONO (20); *β*OCONPh (18) |
| 34 |  | | 708 | 10.6016 | δONO (14); *β*OCCCPh (15) |
| 33 |  | | 693 | 29.1056 | δONO (51) |
| 32 |  | | 657 | 20.1640 | βOCCCPh (17) |
| 31 |  | | 591 | 64.3893 | δCNCPi (16); τHCNCPi (16); τHCCNPi (20) |
| 30 |  | | 545 | 31.4872 | δONC (54); δCCCPh (11) |
| 29 |  | | 538 | 4.7846 | τCCCCPh (28); βOCCCPh (13); βNCCCPh (13) |
| 28 |  | | 525 | 31.1282 | βNCCCPh (15) |
| 27 |  | | 479 | 0.2931 | δCNCPi (24); δCCNPi (23); τHCNCPi (16) |
| 26 |  | | 473 | 127.4816 | νNPi…H (14); δCNCPi (17) |
| 25 |  | | 457 | 30.8087 | δCCCPh (10); βNCCCPh (14) |
| 24 |  | | 419 | 13.1054 | δOCCPh (29) |
| 23 |  | | 415 | 20.2536 | δCCCPh (10); τHCCNPi (10); τCNHPi…N (12) |
| 22 |  | | 403 | 11.4928 | τHCNCPi (10); τHCCNPi (13) |
| 21 |  | | 359 | 8.6147 | δONPh…H (20); δNCCPh (19) |
| 20 |  | | 350 | 1.3746 | νNCPh (12); δCCCPh (14); δCCCPh (13) |
| 19 |  | | 339 | 5.1706 | νNCPh (31); δONO (11) |
| 18 |  | | 335 | 4.0052 | νNCPh (10); δONC (14); τCCCC (14); βOCONPh (13) |
| 17 |  | | 296 | 9.9549 | τHCNCPi (26); τCNCCPi (15) |
| 16 |  | | 295 | 1.9197 | βOCONPh (44); βOCCCPh (10); βNCCCPh (17) |
| 15 |  | | 249 | 0.6410 | τHCNCPi (15); τHCCNPi (25); τCNCCPi (19); τCNCCPi (22) |
| 14 |  | | 208 | 7.1441 | δONPh….H (16); δNCCPh (12); δNCCPh (40) |
| 13 |  | | 199 | 1.6367 | τCCCC (35); βNCCCPh (13); βNCCCPh (12) |
| 12 |  | | 167 | 7.3607 | νNPi…H (13); δNCCPh (50) |
| 11 |  | | 130 | 18.8059 | νNPi…H (30); δNCCPh (22) |
| 10 |  | | 124 | 14.3984 | τCCCCPh (11); βNCCCPh (41) |
| 09 |  | | 108 | 4.8306 | δCNHPi (10); τH…NCCPh (19); τCCCCPh (13); τCCCCPh (11); τONPh…HN (13); τCNHPi…N (13) |
| 08 |  | | 96 | 0.2420 | δCNHPi (11); τH…NCCPh (11); τONPh…HN (49); βOCONPh (13) |
| 07 |  | | 78 | 3.4770 | δH…NCPh (10); τCCCCPh (17); τCCCCPh (11); τCNHPi…N (15) |
| 06 |  | | 76 | 6.4595 | δH…NCPh (21) |
| 05 |  | | 48 | 0.3773 | τONCCPh (90) |
| 04 |  | | 47 | 0.7615 | τONCCPh (83) |
| 03 |  | | 36 | 0.3478 | δNHPi…. N (49); δH…NCPh (21) |
| 02 |  | | 31 | 0.2779 | τH…NCCPh (43); τCNHPi…N (27) |
| 01 |  | | 21 | 0.2481 | τNHPi…NC (64); τH…NCCPh (12) |

*ν*: Stretching; *τ*: Torsion; *ω*: Wagging; *δ*: Scissoring; *ρ*: Rocking; *β*: out–of–plane bending

a [26] exp values

b [47]

c [45]

**The calculation details:**

and

These HRS invariants and are orientational averages of the tensor, and calculated without assuming Kleinman’s conditions. and are defined as [36]:

The full expressions of the can be find in Ref. [60]:

We calculate the orientational averages of the tensor components and

For the invariant :

For the invariant :

after, we detail each sum separately:

The invariant :

*=*

=

=

and the same for the second term .